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PAPERS ON SMELTER SMOKE

BY

W. D. HARKINS AND R. E. SWAIN

Excess-Potential and the Marsh Test

BY

W. D. HARKINS

UNIVERSITY

A Thesis Submitted by W. D. Harkins for the Degree of Doctor of Philosophy

Stanford University
1907

EXCHANGE

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PAPERS ON SMELTER SMOKE.

(FIRST PAPER)

The Determination of Arsenic and Other Solid Constituents of Smelter Smoke, with a Study of the Effects of High Stacks and Large Condensing Flues.

BY W. D. HARKINS AND R. E. SWAIN.

Received May 2, 1907.

The determination of the constituents of smelter smoke is important for two reasons: many of the constituents have considerable commercial value, while a large number are poisonous in varying degrees to plant and animal life. Under the first class will come sulphur dioxide, sulphuric acid, copper, lead, zinc, arsenic, antimony, and certain other substances. It will be seen that these same substances belong in some degree to ehe second class as well, so that the solution of the problem of recovering the economic values from the smoke will also solve the problem of lessening or preventing its injurious action.

It will be the purpose of a series of articles, of which this is the first, to point out the chemical facts which make the solution of these problems so essential to the welfare of many extensive districts in the west, as well as to some in the east and south of our country. The work which led to the publication of this special article, was the estimation of the amount of arsenic expelled from the greatest of the world's smelters—a plant which has a capacity of ten thousand tons of ore per day, and the output of which for 1906 was estimated as eleven and one half per cent. of the world's production of copper. Compare with this the Freiburg smelters at the time of the work of Haubner[1], Sussdorf[2], Freytag[3], taking the date 1870. At this time the two smelters, the Mülden and Halsbräcken, treated daily about seventy tons of ore. According to Haselhoff and Lindau[4], all the smelters of the Lower Hartz use annually only sixty-three thousand tons, this being the amount for the year 1899. In this country, the Garfield Beach smelter, Utah, is to be enlarged to a capacity of eight thousand tons per day, while the Great Falls, Montana, smelter has now a capacity of three thousand five hundred tons

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[1] Haubner, Die durch Hüttenrauch veranlassten Krankheiten des Rindviehes im Hüttenrauchsbezirke der Freiberger Hütten (Arch. f. wiss. u. prakt. Tierheilk. 1878, 4, 97-136; 241-260.)

[2] Sussdorf, Allg. Deut. Naturhist. Ztg., Hamburg, I (1855), No. 3, 97.

[3] Freytag, M., Jahrb. f. d. Berg-u. Hüttenwesen im Königr, Sachsen auf das Jahr. 1873, Abh. 3. ——, (l. c. 1875, Abh. 3).

[4] Haselhoff und Lindau, Rauch-Beschädigung, p. 147.

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per day, and will soon be made much larger. In Nevada, the Ely smelter is to treat from ten to twenty thousand tons of ore per day. Many other great plants could be named, but these examples are sufficient to show that the problem of injury by smoke is a much more important one in this country than it is in Germany, at least in so far as the magnitude of the smelting operations themselves is concerned.

During the last few years there have been numerous complaints from smelter districts, that the trees and grass are not only injured in their growth by the sulphur dioxide and sulphuric acid of the smoke, but in some way the grass is also rendered poisonous for horses and stock, probably as the result of the deposition of mineral poisons. This calls to mind the investigations made in Germany in the year 1849 by Stockhardt,[1] and in 1853 by Stockhardt aud Frange,[1] who decided that the poisoning caused by smelter smoke was due to the action of lead. However, the later investigations of Sussdorff and Haubner, as referred to above, show conclusively that the principal damage was caused by arsenic, and not by lead.

The investigations which led to the publication of this series of articles on smelter smoke, were begun by one of us (Harkins) in the year 1902, about ten months after the completion of the smelter. The smoke and the grasses of the district were found to contain considerable arsenic, while small quantities of this element were found in the organs of herbivorous animals living in the vicinity of the smelter. For many years previous the ore had been treated in a plant which cost in all about six million dollars, but in January 1902 this was abandoned for the present smelter, in order to reduce the cost of smelting by the adoption of improved methods. The stone and brick settling flues, which in the old works served to carry the smoke to the tops of the hills upon which the stacks were built, were in the new works replaced by large condensing chambers of brick. These chambers averaged about forty feet wide, forty feet high, and two hundred and sixty feet long; but the volume utilized in settling the flue dust was somewhat less than this, since ten feet of the height was taken up at the bottom by a passageway for the cars that carry the dust to the reverberatory furnaces. The volume of each chamber was therefore about three hundred thousand cubic feet. One was attached to the roaster building, one to the blast, and one to the converters, and each was provided with a separate steel stack, twenty-two feet in internal diameter, and two hundred twenty-five feet high. The smoke from the reverberatory furnaces was discharged directly into a stack of the same dimensions.

Whether or not the settling chambers were less effective than the long flues of the old works, is very difficult to say; but it certainly is

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[1] Opinion transmitted to the Royal Minister of the Interior, 1854.

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a fact, that during the year after the erection of the new works the loss of animals in the valley became very much greater than before. This was due in part to a difference in the location of the smelters, since the new smelter was built closer to the valley lands, and in such a position that the prevailing winds carried more of the smoke across the farms of the district. Even if it is possible that some of the increased poisonous action of the fields upon the animals was due to a difference in the composition of the smoke, owing to a change in the methods of smelting, still it is certain that much valuable material, somewhat poisonous, was thrown out by the old works. The ground surrounding them became so rich in copper that a very large amount of this metal was obtained by smelting the top soil of a considerable area.

As a result of the operation of the new smelter, the losses of stock in the valley during the year 1902 were so heavy, and the hay and grass, on analysis, showed so much arsenic, that a great system of flues was built in order to settle the copper, and to condense the arsenic trioxide. The latter escaped in large quantities as a gas, especially from the blast and McDougall roasting furnaces. The system of flues built at this time, is the largest in the world, and a study of its effects in settling different compounds presents many interesting chemical problems, only a few of which can be touched upon here.

This first set of flues joins all the furnaces to one great flue, the smoke from three of the buildings passing through the settling chambers before entering the flues at all. Of the connecting flues the blast furnace flue is 1653 feet in length; the reverberatory flue, 842 feet; the roaster flue, 488 feet; and all are twenty feet wide and twenty feet high. The converter flue is at present 703 feet long, 18 feet wide, and 10 feet high. All these join in one great flue, and for twelve hundred feet this is sixty feet in width, with twenty foot side walls. The bottom slopes down on both sides to hoppers in the middle, which open into cars underneath. It is 36 feet from the top of the flue to the bottom of the excavation, and the area of the cross section of this portion is 1600 square feet. Above this there are two parallel sections, each 1000 feet long, and of the same dimensions as the single flue, making a double flue, 120 feet wide, with a cross section of 3200 square feet.

The volume of the original settling chambers is about 900,000 cubic feet, while that added in 1903, in the form of new flues, is about 6,000,000 cubic feet, making the volume available for settling the solids of the smoke practically seven and one half times as great as before. In order to cool the gases, the 120 foot flue is covered with a roof made of thin pieces of sheet steel, supported by I beams underneath. This flue lies on a steep mountain side, and ends at the top in a big stack, 31.33 feet in internal diameter, 44.5 feet external diameter at the bottom, 30 feet internal diameter at the top, and three hundred feet high. The smoke is admitted to the stack by two openings on opposite sides, each 12.5 feet wide by 34.5 feet high. The elevation of the top of the stack is 6,186 feet, and of the reverberatory furnaces, 5442 feet, or a difference of seven hundred feet. The top of the stack is eleven hundred feet above the valley below.

The great flues and stack were built in order to settle the arsenic and copper, and to prevent the damage to the forests and crops from the sulphur dioxide of the smoke. After a year and a half of operation, it was claimed by the smelter company that these results were accomplished, and that practically all of the arsenic was deposited in the flue and chambers, while the stack raised the smoke to such a height that the sulphur dioxide did little damage to vegetation. The farmers of the district asserted on the other hand, that their animals were poisoned, and their crops damaged in the same way as before, though the distribution of the damage was somewhat different.

The velocity determinations and analyses of smoke which follow, and the more recent of the investigations in regard to the crops and animals, as given in the later papers, were undertaken to determine the real efficiency of this flue and stack.

The Determination of Velocity.—In sampling and analyzing smoke, among the most difficult problems is one which may seem to belong to the engineer, but which, our experience has shown, cannot be left to the ordinary man in this profession. Since the results of his analyses depend entirely for their calculation upon the volume of the smoke given off, it becomes the duty of the chemist to make these volume or velocity measurements

In the determination of the velocity of moving gases there are only two methods which have any claim to accuracy. These are the determination by the Pitot tube, and that by the ordinary wheel anemometer. A method much used by smelter men consists in releasing a piece of charred paper, and noting the time which it takes to rise to the top of the stack. This is manifestly a very crude method, and is not applicable in the case of very large stacks, since it is impossible to see the charred paper when it first leaves the top of the stack. Another method sometimes used is to obtain the difference in pressure between the outside and the inside of the chimney.

The Pitot tube was devised by Pitot[1] in 1732, and was used for the determination of the velocity of water. It consisted of an L tube with the ends of the two arms open, but with the horizontal arm drawn down to a small opening. When turned with the horizontal arm pointing up stream, the impact of the stream on its mouth balanced a column of

[1] Pitot, Histoire de l'Académie des Sciences (1732), p. 376.

water in the vertical arm of a height equal to the square of the velocity divided by twice the coefficient of gravity. When the plane of the mouth of the tube was placed parallel to the motion of the stream, the level of the water inside and outside the stream was practically the same. When two tubes are placed thus at right angles with each other and connected with a differential manometer in which the liquid is the same as the moving liquid, the difference of level in the two arms of the manometer is the same as that given above, or $h = \frac{v^2}{2g}$. An instrument of this kind was devised by Darcy, and is known as a Darcy gauge, or a modified Pitot tube.

The principal of the Pitot tube was developed from the proposition of Toricelli[1] by Daniel Bernoulli[2], who used as a basis of his development the principle of the *conservatio virium vivarum.* He proved that in a steady stream of a frictionless liquid, loss of energy of motion is accompanied by an equivalent gain of head, and gain of motion energy by an equivalent loss of head. The head may be in the form of elevation of the liquid or of pressure, or of both combined. In other words, when kinetic energy is converted into potential, or potential into kinetic, the loss of kinetic energy is accompanied by an equal gain in potential energy, and the gain of kinetic energy by an equal loss of potential energy. Expressed in symbols:

$$mgh = \tfrac{1}{2} mv^2$$

or

$$v = \sqrt{2gh}$$

This is the last formula of the Pitot tube, and is the same as the well known formula for the efflux of liquids.

Although there has been considerable dispute as to the practical formula of the Pitot tube, the experiments of Darcy, and also of most of the modern writers, show that in the formula $v = c \sqrt{2gh}$ the factor c is unity within the limits of experimental error, where the tube is of the proper construction. This is the view expressed by Freeman[3], White,[4] liams,[5] Robinson,[6] and Gregory,[7] in recent articles upon this subject. The Pitot tube, when properly constructed, has proved an accurate instrument for the measurement of the velocity of either gases or liquids when the velocities are not too low. Nearly all the early applications of this apparatus were made in the determination of the velocity of liquids, usually the velocity of streams or of ships[1].

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[1] Toricelli, De Motu gravium Projectorum (1643).

[2] Bernoulli, Hydronamica (1738).

[3] Freeman, J. R., Trans. Am. Soc. Civil Engineers, 21 (1889).

[4] White, W. M., J. of Assoc. Eng. Soc., **25** (1900), p. 161, and **27**, (1901), pp. 35-67.

[5] Williams, G. S., Pr. Am. Soc. Civil Eng., May, 1901.

[6] Robinson, S. W., Trans. Am. Soc. Mech. Eng., **25** p. 208-211 (1903).

[7] Gregory, W. B., Trans. Am. Soc. Mech. Eng., **25** (1903).

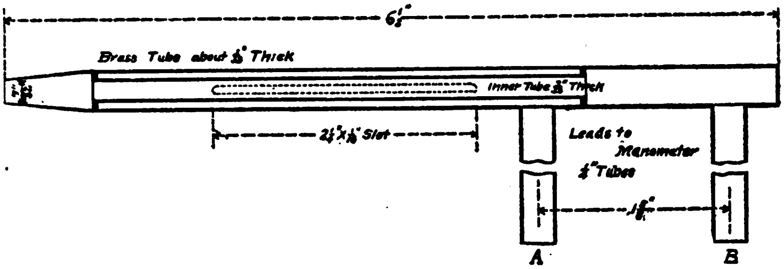

FIG. 1. Pitot tube as modified by Captain D. W. Taylor.

These tubes were made from a design furnished by Captain D. W. Taylor,[2] Naval Constructor at Washington. Tubes of this design had been used by him to test the ventilating fans of the battleship Missouri, and were previously tested by Prof. A. F. Zahm, of the Catholic University, Washington. Using the formula $v = \sqrt{2gh}$, the latter found that the results agreed with very accurate independent measurements of the volume of the air.

The tubes used for our work, as shown in Figure 1, consists of two concentric tubes, each connected to one arm of a differential manometer, so that the latter gives the difference of pressure of the gas in the two tubes. The axis of the tube is placed parallel to the direction of motion of the smoke, and the inner tube has an opening 0.553 centimeters in diameter with its plane at right angles to the axis. The outer tube has a slot 5.71 centimeters long by 0.16 centimeters wide on each side, so that it gives to the manometer the static pressure of the gas. The inner tube corresponds to the original Pitot tube, and gives the static pressure plus the pressure caused by the impact of the gas upon its mouth, or what is often called the velocity pressure. The use of slots instead of the circular openings usually employed to obtain the static pressure, prevents the aspirating effects noticed in the ordinary form of the tube. The two tubes (A) and (B), each 0.63 centimeters in diameter, are provided with screw threads at the ends, and on these tubes iron pipes of the same diameter are fastened. In the velocity determinations these pipes varied in length up to twenty-three feet, and served to support the Pitot tubes in the stack and to connect it with the manometer. To make the support rigid they were stiffened by a band of steel, 1.3 centimeters thick and 4 centimeters wide, which fitted exactly between the two pipes (A) and (B). The pipes and the steel band were bound at distances of 60 centimeters by clamps of heavy steel, bolted together by 1.3 centimeter bolts. It was essential that these supports should be rigid, since the portions inside the wall of the stack had to be entirely self-supporting.

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[1] Berthon, E., The Engineer (1850); Pendred, Vaughn, The Engineer, Dec. 17, 1869; Rankine, W. J. M., The Engineer, Jan. 1870.

[2] Taylor, D. W., Eng. News, 52, 18, p. 387-89, Nov. 3, 1904.

The manometer[1] used for this work was the simplest form possible and proved perfectly satisfactory. It consists of a glass U tube of a small even bore, laid upon the slant of a triangle having a base of 23.74 centimeters, a vertical side of 2.5 centimeters, and a slanting side of 25 centimeters. This was built of well seasoned wood, very carefully cut, and was fastened upon a broad horizontal base into which two levels were set. The U tube was bound down by copper wires, and a steel scale, accurate at 15°, was placed between the two arms. The two sides should be connected at the bottom by a horizontal spiral of the same glass tube, in order to lengthen the natural period of vibration of the ether column. The liquid used was ether, which responds freely to any change of pressure. It had a specific gravity of 0.7300 at a temperature of 17°. The manometer was connected to the Pitot tube pipes through two two-way cocks; and on reversing both of these, the impact arm of the manometer became the static pressure arm, so that the effect of any slight difference of level between the two side tubes was eliminated. Great care was taken to set the instrument in such a way that the two ends of the base of the triangle should be at the same level. For each reading the stopcocks were reversed several times, the average taken, and reduced to velocity by the formula, $V = \sqrt{\frac{2ghD_{\text{ether}}}{120\ D_{\text{gas}}}}$, where h is the reading expressed in inches.

Comparison of a Pitot Tube with an Anemometer.[2]—In order to see how the results obtained by the Pitot tube would compare with those given by a wheel anemometer, the two instruments were placed side by side, as shown in Figure 2. The pipe (A), running just beneath the concrete floor, connects a large fan, placed some distance from the section shown in the cut, with one of the main flues of the building where the tests were made. The Pitot tube (P) and the anemometer (M) were supported by the two 0.64 centimeter iron pipes (C), which connect with the two arms of the Pitot tube—the static pressure arm (S), and the impact arm (I). The tubes (C) were connected by the rubber tubes (R) to the differential ether manometer. The anemometer was stopped or started by the lever (L″), which was turned by means of a series of levers and rods (L,D,L′ and D′), arranged so that the recording mechanism could be turned on or off without removing the apparatus from its place. The Pitot tube (P) and the anemometer (M) were set so that their axes were at equal distances from the axis of the pipe. The whole

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[1] Seger's manometer may be used if a vertical form of instrument is desired.

[2] The anemometer was the property of the Department of Mechanical Engineering of Stanford University, and was the best instrument which could be purchased. The apparatus used for this purpose was designed for us by Professor W. R. Eckhart, Jr.

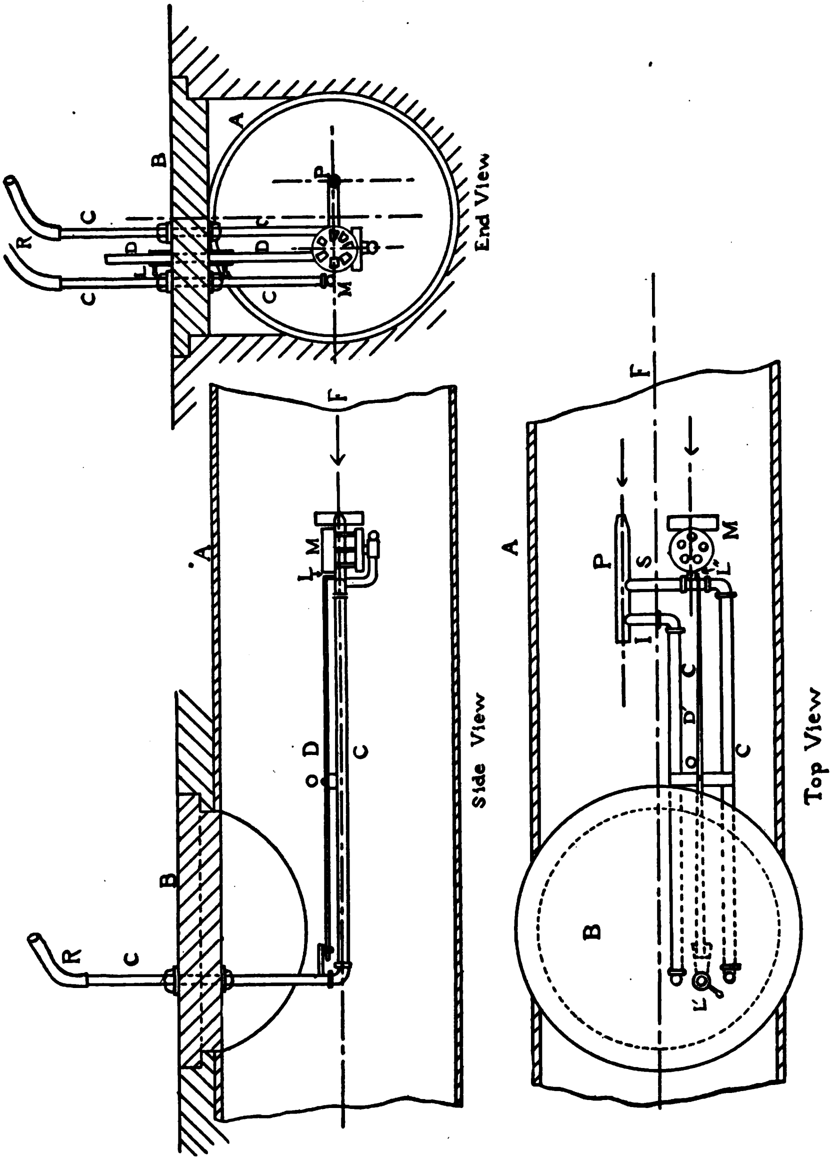

FIG. 2.

apparatus being supported by the tubes (C), which were fastened in the removable cover (B) of the manhole, could be removed in a moment to read the anemometer. The instruments were set several feet from the manhole so that the slight irregularities in the pipe at the latter would cause no eddies near the instruments.

The apparatus was put in place, and the fan regulated until the manometer of the Pitot tube indicated that the velocity of the air had become as nearly constant as possible. The recording mechanism was then turned on, and the readings of the Pitot tube manometer taken for a certain time, usually five minutes. The recording mechansim of the anemometer was then stopped, the apparatus taken out, and the dial read. The fan was run at the highest and lowest velocities possible, as well as at numerous intermediate velocities. The determinations as shown in Table 1[1], are not given in the order in which they were made, but are rearranged in the order of the increasing velocity.

The column "Ft. per Second Corrected" gives the results as determined by the anemometer, corrected by the calibration curve of the instrument maker. Under $\frac{V_{\text{anemometer}}}{V_{\text{pitot}}}$, the first column gives the anemometer velocity as obtained directly by reading the dial, divided by the velocity as determined by the Pitot tube. In the second column the anemometer reading has been corrected by its calibration curve.

On account of this rise of reading with the velocity, the easy corrosion of its parts, the fact that in the smoke the vanes become loaded with flue dust, and its high original cost, the wheel anemometer is a very poor instrument for the determination of the velocity of smelter smoke. The cost is of importance, since a number of instruments should be used.

Determination of the Velocity Curve.—The sampling hole, through which all our apparatus was introduced into the stack, was 5.75 inches in diameter, formed by an iron pipe extending through the five-foot wall, and projecting one foot on the outside of the stack. It was 53 feet from the ground, at an altitude of 5935 feet, and about 13 feet above the top of the baffle wall, which extends across the middle of the stack. At the time our measurements were made, we believed that the top of the baffle wall was very much lower than it really is, so at that time we were not able to understand why our curve of velocity showed a velocity considerably lower at the center of the stack than at four feet from the inner wall. The sampling hole was the highest opening in the stack, and also the only opening at this height, so that we were able to secure no other support for our apparatus than its walls. Not only the small size of this opening, but also its length, and the fact that it was round, made it difficult to insert, and keep vertical, any large amount of apparatus for the velocity determination. When no smoke sample was being drawn off, it was possible to insert four tubes for the

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[2] The calculations in this table, and all the other calculations in this paper, were made on a slide rule.

TABLE I. Comparison of an Anemometer and a Pitot Tube.

$$V_{P.\,tot} = \sqrt{2gh\,\frac{D_{ether}}{D_{air}}}$$

$2g = 64.28$ $b = 759$ mm $e = 12.7$ mm.

	Anemometer							Pitot.								
No.	2nd Reading Anemometer	1st Reading Anemometer	Difference	Time Minutes	Ft. per minute	Ft. per second	Ft. per second corrected	Pitot Manometer average	Pitot pressure in feet vertical	Temperature °C.	$1 + .003665\,t$	$\frac{.0012934}{1+.003665\,t} \times \frac{759-{}^{3}/_{8}e}{;60}$ Dair	$\frac{D_{ether}}{D_{air}}$	Velocity by Pitot $\frac{Ft}{Sec}$	$\frac{V\ anemometer}{V\ Pitot}$ Readings	$\frac{V\ anemometer}{V\ Pitot}$ Corrected
1	97,606	97,030	576	1	576.0	9.60	9.55	0.312	.00260	16 5	1.0605	.001209	603.0	10.03	0.957	0.952
2	101,108	97,606	3,502	5	700.4	11.67	11.55	0.383	.00319	15.8	1.0578	.001213	602.5	11.15	1.047	1.036
3	291,046	286,554	4,492	3	1497.3	24.95	24.45	1.547	.01289	22.0	1.0807	.001188	615.0	22.52	1.107	1.085
4	286,554	280,905	5,649	3	1883	31.38	30.75	2.320	.01933	22.0	1.0807	.001188	615.0	27.49	1.142	1.118
5	124,813	112,924	11,888	5	2377	39.63	38.84	3.437	.02864	18.4	1.0674	.001203	608.0	33.42	1.186	1.162
6	272,947	265,075	7,872	3	2624	43.73	42.86	4.375	.03646	22 5	1.0824	.001189	616.0	37.92	1.153	1.130
7	280,905	272,947	7,958	3	2653	44.22	43.34	4.445	.03704	22.5	1.0824	.001189	616.0	38.28	1.156	1.132
8	154,580	140,030	14,550	5	2910	48.50	47.54	4.954	.04128	20.8	1.0762	.001193	612.0	40.30	1.203	1.179
9	169,142	154,580	14,552	5	2910	48.50	47.54	5.023	.04186	20.8	1.0762	.001193	612.0	40.58	1.196	1.172
10	184,005	169,142	14,863	5	2972	49.53	48.54	5.198	.04332	21.3	1.0781	.001190	614.0	41.28	1.200	1.176
11	199,463	184,005	15,458	5	3092	51.53	50.50	5.682	.04735	22.8	1.0836	.001185	616.8	43 30	1.190	1.167
12	140,074	124,813	15,621	5	3052	50.87	49.84	5.940	.04950	21.1	1.0773	.001191	613.1	44 12	1.153	1.130
13	218,219	208,730	9,487	3	3162	52.70	51.65	5.922	.04935	22.8	1.0836	.001185	616.8	44.30	1.190	1.166
14	208,730	199,463	9,267	3	3089	51.48	50.45	5.917	.04931	23.0	1.0843	.001184	617.0	44.21	1.164	1.142
15	238,555	228,516	10,039	3	3346	55.77	54.66	6.813	.05677	22.8	1.0836	.001185	616.8	47.42	1.176	1.153
16	228,516	218,219	10,297	3	3432	57.20	56.16	6.877	.05731	22.8	1.0836	.001185	616.8	47.63	1.201	1.178
17	254,096	213,128	10,968	3	3656	60.93	59.71	7.553	.06294	23.0	1.0843	.001184	617.0	49 93	1.236	1.211
18	265,075	254,096	10,979	3	3659	60.98	59.76	7.677	.06397	23.4	1.0857	.001183	617.3	50.36	1.211	1.197

determination of the velocity curve. The region near the wall of the stack is by far the most important in this determination. Thus one-half of the area of the cross section, with its radius of 15.67 feet, is within 4.66 feet of the wall, and also includes all that portion in which there is any great variation in the velocity. Measurements were made at the following distances from the inner wall of the stack, the numbers being given in feet: 0.0, 0.25, 0.50, 0.75, 1.0, 1.50, 2.00, 2.50, 3.00, 4.00, 10.00, and 15.67.

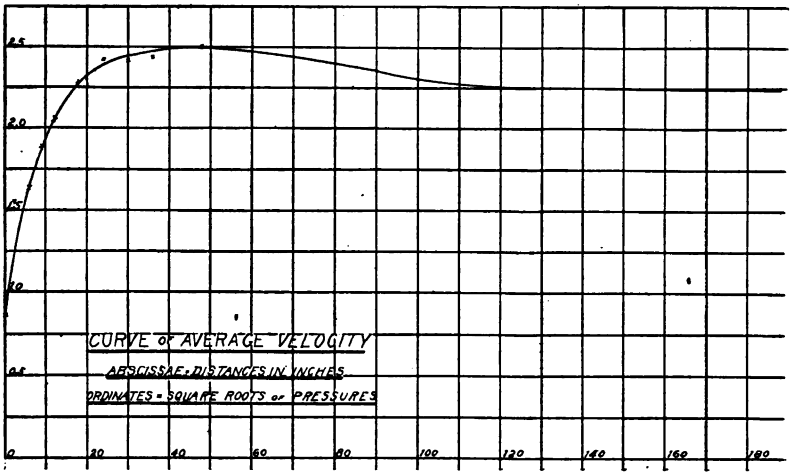


FIG. 3.

The results of these measurements are given in the form of a curve in Figure 3. Instead of plotting the velocities themselves, the square roots of the Pitot readings, multiplied by four, are given as ordinates, and distances from the inside wall as abscissæ. The extreme right of the curve represents the center of the stack. In computing the velocity for the time while samples of smoke were being taken for analysis, determinations were recorded at only one point, the point of maximum velocity, or four feet from the inside wall. This series of determinations was corrected by the velocity curve in order to give the average through the whole cross section. In computing this the method of sections was used. The radius of the stack was divided beginning at the center, into divisions of ten inches each; and the area of the ring formed by each segment, on rotating the radius in a plane about the center of the stack as an axis, was multiplied by the average velocity for that ring as shown by the curve.

Let $a = 10''$ $r_0 = 188''$ $r = 180''$ V = average velocity. Then since

$$V\pi r^2 = V_0\pi[188^2-180^2]+V_1\pi[r^2-(r-a)^2]+V_2\pi[(r-a)^2-(r-2a)^2]+ \\ \dots\dots\dots\dots + V_n\,\pi\,[\{r-(n-1)a\}^2-(r-na)^2]$$

$$V = \frac{1}{r^2}[V_0\,(188^2-180^2)+a\{V_1\,(2r-a)+V_2\,(2r-3a)+V_3(2r-5a)+ \\ \dots\dots\dots\dots + V_n\,(2r-(2n-1)a\}]$$

The calculation according to this formula is shown in Table 2.

TABLE 2

	V.	$2r-(2n-1)a$.	Product.	Product times a
V_0	6.00			17760.
V_1	8.40	350	2940.	29400.
V_2	9.53	330	3146.	31460.
V_3	9.83	310	3046.	30460.
V_4	9.95	290	2885.	28850.
V_5	9.92	270	2678.	26780.
V_6	9.77	250	2442.	24420.
V_7	9.53	230	2192.	21920.
V_8	9.31	210	1955.	19550.
V_2	9.18	190	1744.	17440.
V_{10}	9.08	170	1544.	15440.
V_{11}	9.01	150	1352.	13520.
V_{12}	8.98	130	1167.	11670.
V_{13}	8.96	110	986.	9860.
V_{14}	8.94	90	805.	8050.
V_{15}	8.93	70	625.	6250.
V_{16}	8.93	50	446.	4460.
V_{17}	8.93	30	268.	2680.
V_{18}	8.93	10	89.	890.
			Total =	320880.

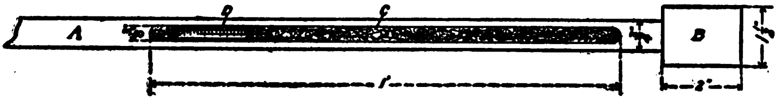
$320880 \times \frac{1}{r^2} = \frac{320880}{35360} = 9.076$, or four times the average square root of the Pitot reading for the whole cross section of the stack. The average square root of the Pitot reading therefore = 2.269.

These measurements covered a period of eight and one-half hours. The average velocity corresponding to the average square root of the Pitot reading (2.269) is 55.80 ft. per second, which gives a volume of 3,721,000,000 cu. ft. in twenty-four hours under the conditions assumed to exist in the stack: temperature= 174.7° C, and pressure=612.2 mm. Under external conditions of $t=17°$ C, and $p=612.2$ mm., the volume would be 2,411,000,000 cubic feet; and under standard conditions, 1,828,000,000 cubic feet. Although the results have been calculated to the same internal and external pressures, the external pressure exceeded the internal by about 5 mm. Other tests will be given later which covered a greater period of time. The curve at 4 feet from the inside wall shows 9.95 as four times the square root of the Pitot reading. The average for the whole cross section of the stack, 9.076 divided by 9.95, the value at 4 feet, gives the factor 0.912. The average velocity over the whole cross section of the stack is therefore 0.912 of the maximum velocity, or the velocity at a distance of 4 feet from the inside wall. This factor is used later in converting velocity at this point into average velocity.

It had been planned to use sixteen tubes in the determination of the velocity of the smoke, but this method had to be abandoned on account of the small size of the opening through which the tubes were introduced. However, the arrangement will be described as it was planned, since it is a somewhat better method than the one we were forced to use. Sixteen tubes are placed in one cross section of the stack in the form of a spiral, each tube at an angle of seventy-two degrees from its neighbors on the spiral. On account of the much greater area of the outer rings when the cross section is divided into concentric rings of equal width, the greater part of the tubes should be near the wall of the stack. In order to obtain the true average Pitot pressure (h), allowance should be made for this fact by some method which depends upon the law, that the area of a circle is proportional to the square of its radius. If the radius is squared and this square divided into fifteen equal parts, the proper distance of the tubes from the center are found by extracting the square root of each of the numbers obtained in this way. For example, in the case of a stack with a radius of fifteen feet the numbers would be: 0, 15, 30, 45, 60, 75, 90, 105, 120, 135, 150, 165, 180, 195, 210 and 225. When the square roots of these numbers are taken, the distances of the tubes from the center are found to be as follows: 0, 3.87, 5.48, 6.71, 7.74, 8.66, 9.48, 10.24, 10.95, 11.62, 12.24, 12.83, 13.40, 13.95, 14.48, and 15. It would be even better to use nineteen tubes at distances of eighty degrees. All the tubes are connected through large air chambers (one for each arm of the manometer) to a differential manometer, or floating manometers may be used according to the method given by Captain Taylor. When this plan is followed, a mechanical average of the pressure through the stack is obtained, taking into account the greater area of the outer rings. The air chambers should be connected to the Pitot tubes so that there are separate connections provided with stop cocks for each tube. In this way readings may be taken on any one, or on all at the same time. The pressure given by the tube in contact with the wall of the stack is so low that it should not be connected with the manometer when the mechanical average is being taken, for it influences too greatly the pressure in the chambers. The greatest error in this method of obtaining a mechanical average is due to the fact that the average velocity obtained is not the true average velocity, but the square root of the average of the squares of the velocities. Still, the results obtained are so nearly correct that they are satisfactory for most purposes. If the relation between these quantities is desired, it can be determined by the apparatus as described above. Since the method would be obvious to a worker who could do work sufficiently accurate to need such a relation, only a bare outline of the procedure will be given. The readings of the separate tubes should be taken in order, one at a time, as rapidly as possible, and this procedure repeated a number of times. After each is read separately, a reading should be taken with all the tubes connected, except those that have not been included in the mechanical average. The single readings should then be calculated to velocity, and curves drawn showing its variation with the distance from the wall of the stack. From these can be calculated the average velocity by the method given later, or by any other satisfactory method. These results should then be compared with the results from the mechanical averages which were obtained under the same conditions. The ratio will serve for the correction of all the mechanical averages obtained during the drawing off of smoke samples. A simpler method would be to use the tubes singly in determining the velocity curve according to the method given by Figure 3 and the accompanying description.

Measurement of the Temperature.—The temperature was measured by the simplest means possible, which, while not so satisfactory as a good self-recording instrument[1], gave accurate measurements for the times that the readings could be taken. An accurate chemical thermometer was put in a long iron pipe A, Figure 4, with the bulb of the thermometer wrapped carefully in asbestos. The bulb was protected by an iron cap (B), two inches long and one and one-half inches in diameter. The whole stem of the thermometer, except the portion to be read, was wrapped in asbestos, and then the small exposed portion of the scale was covered with a loose layer of the same material. The scale of the thermometer could be read through a long slot (C) in the wall of the pipe. Before beginning the readings, the bulb (B) was put in the desired location in the stack, and left there for one hour. The pipe was then very quickly partially withdrawn, until the portion of the thermometer to be read (D) was just outside the sampling hole. This portion was quickly uncovered and the reading taken; then the scale was at once recovered and the instrument immediately inserted in the stack. Subsequent readings could be taken every fifteen minutes.

FIGURE 4 Scale ¼ Size



Velocity Measurements for the Smoke Samples.—Sample 4 was taken during a period of twenty-eight hours. Preparations had been made for a seventy-two hour run, but a violent thunderstorm stopped the work at the end of twenty-eight hours. The data and results of the velocity determinations for this sample are given in Table 3.

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[1] A recording resistance thermometer may be used near the wall of the stack.

TABLE 3.

VELOCITY OF THE SMOKE.

$$V = \sqrt{2gh \frac{D_{ether}}{D_{gas}}}$$

Density of Ether = 0.7300

Density of Gas = 1.018 × Density of Dry Air.

	Pitot Reading.	Temperature.	*h* Feet	$D_{air\ dry}$	Velocity ft. per sec.=V
Aug. 23,'05					
A.M. 11.45	5.00	177	.04167	.0006312	55.05
12.45	4.75	177	.03960	.0006312	53.75
P.M. 1.45	5.25	173	.04375	.0006365	56.22
2.40	5.25	173	.04375	.0006365	56.22
3.00	7.00	173	.05833	.0006365	64.96
3.50	5.50	173	.04583	.0006365	57.60
4.30	6.00	173	.05000	.0006365	60.16
4.45	5.50	174	.04583	.0006350	57.64
5.00	6.50	177	.05416	.0006312	62.88
5.20	6.50	178	.05416	.0006298	62.96
3.40	6.25	174	.05208	.0006350	61.41
6.00	6.00	177	.05000	.0006310	60.43
6.10	7.00	176	.05833	.0006324	65.20
6.30	6.50	174	.05436	.0006350	62.76
6.50	7.00	180	.05833	.0006266	65.45
7.20	6.50	170	.05436	.0006406	62.52
7.55	7.50	172	.06250	.0006379	67.19
8.05	8.00	172	.06667	.0006379	69.40
8.20	8.25	176	.06867	.0006417	70.75
8.45	7.75	174	.06460	.0006350	68.42
9.15	7.00	173	.05833	.0006365	64.95
9.45	7.00	174	.05833	.0006350	65.00
10.00	7.00	174	.05833	.0006350	65.00
10.20	7.00	175	.05833	.0006329	65.13
11.15	6.00	180	.05000	.0006265	60.56
11.40	6.25	170	.05208	.0006409	61.16
A.M. 12.05	6.50	175	.05416	.0006329	62.75
12.15	6.50	180	.05416	.0006265	63.07
12.30	6.25	175	.05208	.0006329	61.54
12.50	6.50	174	.05416	.0006350	62.66
1.30	7.25	180	.06040	.0006265	66.70
2.00	8.00	175	.06667	.0006329	69.49
2.30	8.00	179	.06667	.0006283	69.95
3.30	7.00	174	.05833	.0006350	65.03
4.20	7.25	170	.06040	.0006409	65.86
4.45	7.50	171	.06250	.0006398	67.15
5.15	7.25	169	.06042	.0006423	65.82
5.45	7.00	165	.05833	.0006481	64.41
6.20	6.50	160	.05416	.0006557	61.65
6.40	6.00	158	.05000	.0006585	59.17
7.10	7.00	165	.05833	.0006484	64.41
7.25	8.00	166	.06667	.0006470	68.87

Time.	Pitot Reading.	Temperature.	*h* Feet	$D_{\text{air dry}}$	Velocity ft. per sec.=V
8.05	8.50	173	.07083	.0006363	71.58
8.25	9.00	173	.07500	.0006363	73.65
9.20	8.50	175	.07083	.0006265	71.76
9.55	9.25	180	.07708	.0006329	75.22
10.45	9.50	185	.07916	.0006200	76.63
10.55	9.40	180	.07837	.0006265	75.84
11.05	9.40	180	.07837	.0006265	75.84
11.15	8.50	175	.07083	.0006329	71.75
11.20	9.50	175	.07916	.0006329	75.84
11.30	9.75	185	.08124	.0006200	77.64
12.00	8.75	178	.07294	.0006296	73.40
P.M. 12.25	9.00	177	.07500	.0006310	74.01
12.40	9.25	185	.07708	.0006200	75.65
1.00	8.75	183	.07294	.0006245	73.36
1.30	9.00	187	.07500	.0006175	74.78
2.00	8.50	171	.07083	.0006394	71.42
2.15	8.50	171	.07083	.0006394	71.42
2.32	9.00	180	.07500	.0006265	74.22

$g=32.158$ Average Gas Pressure=612.2mm.[1]

Pitot tube at 48 inches from the inside wall of the stack.

The average velocity was obtained by plotting the results given in this table as ordinates and the time in hours as abscissæ, which gave the curve shown in Figure 5. The average velocity was found by obtaining the area of the curve with a planimeter, and dividing this area by the horizontal distance across it. The result obtained in this way is 65.00 feet per second. From this the average velocity for the whole cross section of the stack is 59.24 feet per second, or 65.00 multiplied by 0.912, the factor for conversion into average velocity, and the volume per day at the temperature of the stack, 3,098,000,000 cubic feet. At the temperature of 17° (the average temperature of the surrounding air) the volume would be 2,007,000,000 cu. ft., and under standard conditions, 1,523,000,000 cu. ft.

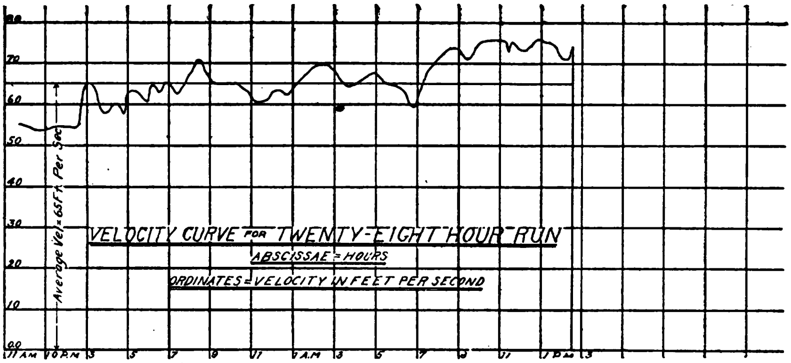

FIG. 5

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[1] On account of the breaking of our standard barometer during transit by express, an aneroid barometer had to be used in taking the pressures.

The average velocity for smoke sample 2 was found in exactly the same way, the data being given in Table 4. On account of an accident to the velocity determination apparatus, there is a considerable break in the readings between 8.30 and 12 A. M.

TABLE 4 (Sample 2).—VELOCITY OF SMOKE.

July 23, 1905. $p = 613.4$ mm.

Time.	Pitot.	T.	h Feet	$D_{\text{air dry}}$	V.
A.M. 1.00	7.25	182	.06038	.0006264	66.64
1.15	7.00	182	.05828	.0006264	65.45
2.00	6.75	182	.05624	.0006264	64.34
2.50	6.50	182	.05414	.0006264	63.14
3.30	6.25	182	.05204	.0006264	61.84
4.10	5.50	182	.04580	.0006264	58.01
5.10	5.50	182	.04580	.0006264	58.01
6.10	5.25	182	.04372	.0006264	56.63
6.36	5.00	182	.04165	.0006264	55.36
8.30	4.75	181	.03957	.0006276	53.85
12.00	3.25	181	.02708	.0006276	44.58
P.M. 3.15	3.00	181	.02500	.0006276	42.85
3.35	3.20	181	.02666	.0006276	42.29
3.50	3.50	181	.02956	.0006276	46.28
4.00	4.00	181	.03332	.0006276	49.44
5.10	3.00	181	.02500	.0006276	42.85
6.00	2.50	181	.02092	.0006276	39.10
7.15	3.25	180	.02708	.0006294	44.57
7.50	4.00	179	.03332	.0006306	49.37
8.15	4.50	178	.03750	.0006308	52.34
8.45	5.00	177	.04163	.0006334	55.04
9.15	5.00	176	.04163	.0006346	55.03
9.45	4.50	175	.03750	.0006361	52.15
10.00	4.00	174	.03332	.0006376	49.10
10.25	4.50	174	.03748	.0006376	53.07

The average velocity as calculated from the curve, Fig. 6, is 50.90

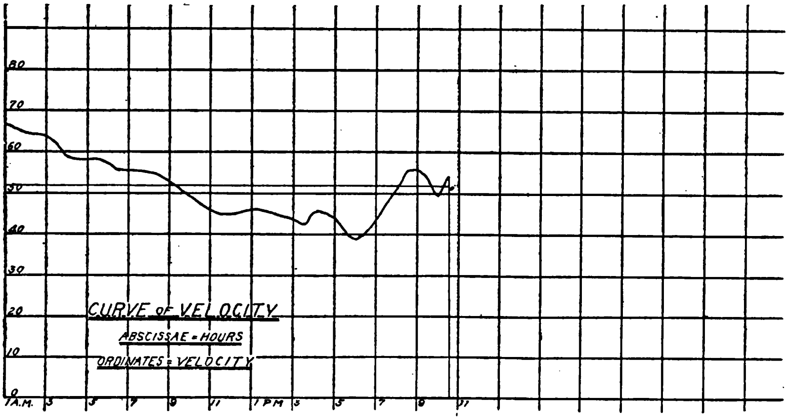

FIG. 6.

feet per second; this multiplied by the factor 0.912, gives the average velocity for the whole cross section of the stack as 46.43 feet per second. The volume at the temperature of the stack in cubic feet per day is 3,098,000,000;under the conditions of the outside air, 2,007,000,000; and under standard conditions, 1,523,000,000.

Another smoke sample was taken on July 27, 1905, the measurements being made four feet from the inner wall of the stack, and under an average pressure of 616 mm. The results of the velocity measurements are given in Table 5.

TABLE 5 (Sample 3).—VELOCITY OF SMOKE.

July 27, 1905. $p = 616$ mm.

	Time.	Pitot inches	T	h Feet	$D_{\text{dry air}}$	v
A.M.	8.40	4.00	189	.0333	.0006187	49.80
	8.55	4.00	189	.0333	.0006187	49.80
	9.30	4.25	189	.0354	.0006187	51.38
	10.00	4.50	189	.0375	.0006187	52.85
	10.35	4.75	189	.0396	.0006187	54.32
	11.10	4.75	190	.0396	.0006076	54.40
	11.45	5.00	189	.0416	.0006187	55.63
P.M.	12.45	5.00	188	.0416	.0006292	55.58
	1.30	5.00	187	.0416	.0006018	55.55
	2.20	5.50	188	.0458	.0006202	56.44
	3.10	4.75	189	.0396	.0006187	54.32
	3.45	4.75	191	.0396	.0006148	54.46
	5.00	5.25	189	.0437	.0006191	57.02
	6.00	5.25	188	.0437	.0006292	56.98
	6.15	5.00	187	.0416	.0006018	55.58

The average velocity is 54.86 feet per second, or 50.04 feet per second for the whole cross section of the stack. The volume of the smoke per day is 3,337,000,000 cubic feet at the temperature of the stack; 2,092,000,000 cubic feet at the temperature of the outer air (17°) ; and 1,595,000,000 cubic feet at standard conditions.

A summary and average of the volume determinations will be given later in the paper.

Standardization of the Meter.—A recording wet meter would have been used for this work if it could have been procured in time, but the best instrument available was of the type of dry meter used for measuring the volume of illuminating gas.

The great inconvenience of this type is that for small volumes it is necessary to keep track of the movement of the hand which gives the number of cubic feet and fractions, since the recording hands do not move with sufficiency accuracy. This is not so great an inconvenience as it seems, for in any case it is necessary to note constantly the velocity at which the smoke is passing through the sampling apparatus. The meter was tested by displacing the air from a large gas holder by the addition of water. Several tests were made in this way, the gasholder being connected with the meter, and the latter to a filter pump. The meter was tested at various pressures, the pressure in the apparatus being determined and kept constant by means of a T tube which was interposed between the meter and the gas holder. The lower arm of this T tube was graduated in millimeters, and dipped into a cup of mercury. In the later experiments the gasholder was replaced by a fifty gallon tank, into which measured amounts of water were introduced from a large carboy. The results are shown in Table 6.

TABLE 6.—AIR DRAWN THROUGH METER.

Test	Pressure.	Meter Cu. Feet.	Gasometer Cu. Ft.	Correction Cu. Ft.	Correction Per Cent.
1	580 mm.	14.25	14.44	+ 0.19	+ 1.31
2	430 "	22.00	22.32	+ 0.32	+ 1.43
3	500 "	16.00	16.19	+ 0.19	+ 1.17

The average correction of the meter reading was taken as 1.3 per cent. Experiments at pressures slightly over 760 mm. gave practically the same correction.

Apparatus for Collecting Samples of Solids.—In sampling smoke for solids there are a few general principles which should be observed in the design of the apparatus for the work. The apparatus recommended for this purpose is shown in Fig. 7, of which the apparatus used by us in our work is a modification. The gas should pass through the opening (O) of the sampling tube at the same velocity as that of the surrounding smoke, which may be as great as 75 feet per second, or 4,500 feet per minute, according to the data given in Table 3. The flue dust tends to collect to some extent around the edge of the opening (O), and if this is very small, may change the diameter so materially that it is difficult to calculate the velocity through it. If this factor alone were considered, the opening (O) would be made large; but, since the volume of the smoke which passes through the sampling apparatus varies as the square of the diameter of the tube, the practical limit must be small, unless the apparatus is made exceedingly large. The apparatus as shown in Figure 6 is intended for an opening 0.60 to 1.00 centimeter in diameter. When the opening is of this size, the apparatus must be large, if the velocities encountered are as great as those in our experiments. The tube (B) through which the smoke first passes after leaving the stack, is shown as eight centimeters in diameter, and the rest of the apparatus in proportion; though if convenient, it would be better to have this one tube (B) even larger.

In the case of sample Number 4, (A) was a Jena hard glass tube, 24 feet long, supported and protected by an iron pipe in which it was placed. A porcelain lined iron tube was tried in the case of sample 1 (which has not been given), but this was unsatisfactory as the porcelain

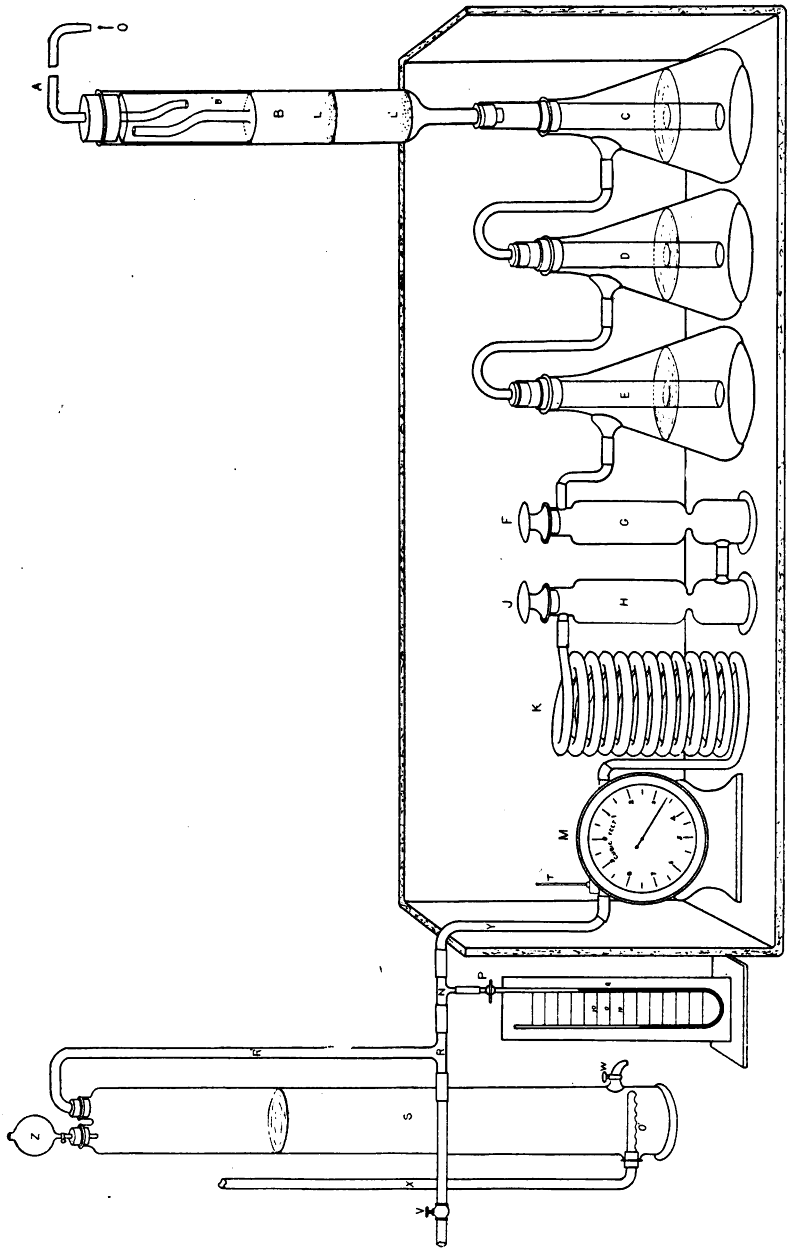

FIG. 7. Apparatus for Collecting the Solids of Smoke.

lining cracked. (B) is a large tube of thin glass, having projections on the inside for the support of other apparatus; B′, a glass cup[1], designed to catch any heavy dust which may pass through the tube A; L and L′ are porcelain discs upon which ash free absorbent cotton is piled loosely. The gas next passes through three large filter flasks (C,D, and E), then through two bottles (G and H) filled with absorbent cotton; and finally, just before entering the meter, through a coil of thin copper tubing in order to equalize the temperature. This apparatus, including the meter, is contained in a box in which all the apparatus may be carried. The box is made water tight, so that water may be kept running through it in order to maintain a constant temperature. A window just in front of the dial of the meter, makes the reading of the latter easy, while a cover having openings for the tubes (B) and (Y), protects the apparatus while in use and during its transportation. After passing the meter, the gas is drawn off through an iron pipe. The pressure is partially regulated by the valve (V) in the pipe, and is measured by the manometer (Q), being finally determined by the height of the liquid (mercury or water) in the regulating tower (S). The exhaust through the valve (V) is always kept just strong enough to cause a small amount of air to pass down the tube (X), through the openings (O′), the column of liquid in (S), and the tube (R) into the T tube which forms a portion of the main exhaust pipe. Liquid may be added to the tower (S) by the dropping funnel (Z), or drawn off through the outlet (W). The three filter flasks contain water or some other liquid absorbent; and although not shown in the drawing, the lower portions of the tubes (C), (D), and (E), are pierced by a large number of small holes. The connections are made by rubber stoppers and by rubber tubes which have been first soaked in strong caustic potash solution, then in water, and finally in paraffin. Glass stoppers are not so satisfactory, since they sometimes begin to leak suddenly; and they weaken the apparatus, making it less flexible. Large rubber stoppers have the base covered by a disc of glass. Other parts may easily be added to the apparatus, such as a large trap to catch the solids just before they pass into B, in order to decrease the clogging of the absorbent cotton by dust.

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[1] This is omitted, if the total weight of dust is not desired. A simple cup, without the inside tube, would serve as well and be less fragile. It is supported by platinum wires.

It will be found, on using a properly constructed apparatus, that the greater portion of the heavy solids will deposit before reaching the absorbent cotton; however, it will be necessary to insert the trap in (A) if high velocities are to be used.

In our work we used a smaller opening (O) of the sampling tube, and found that in a short time the maximum amount of flue dust collected at its mouth, the high velocity at this point keeping it from filling up to any extent. Still, the larger opening is advised, since its free diameter can be calculated with more certainty. The opening should be of platinum foil, or of a sharpened glass tube. If it is desired that the mouth of the sampling tube should be placed in different portions of the cross section of the stack for different periods of the time of sampling, this may be accomplished by making the portion of the sampling tube (A) which lies outside the stack in several joints.

It will often be advisable to use the apparatus in a simplified form, in which case the tube (B) may be made from a condenser jacket simply filled with cotton. This was the form of apparatus used in the work given in this paper, and it proved very satisfactory. However, the glass tube (A) was so long that it rendered the use of a cup or a trap unnecessary, as will be shown by the data on Sample 4.

Determination of the Total Weight of the Solids.—In determining the total weight of the solids contained in a certain volume of the smoke, as great a quantity of the dust as is possible should be collected before the smoke reaches the absorbent cotton. Asbestos fiber may be used in the place of the cotton, but the latter is more efficient in stopping the finer particles. A large amount of the solids can be shaken out from the tubes (A) and the cup (B′) and weighed without further treatment. The whole inside of the apparatus should then be washed[1] with water, the solution filtered and evaporated. The residue from the evaporation and that on the filter paper (or better, in the Gooch crucible) is first dried [illegible] then w[illegible]hed. The remainder of the solids may then be washed out by aqua regia, the solution evaporated, the residue dried and weighed. The cotton, which should be of a known weight and ash content and as ash free as possible, is decomposed by nitric and sulphuric acids until the organic matter is entirely destroyed, then the solution is evaporated, and the residue dried and weighed. Although a portion of the dust is changed somewhat in chemical composition by the action of the solvents, the results are sufficiently accurate. The total weight of the dust may be checked by a complete analysis of the residues.[2]

The Collection and Analysis of the Samples.—Sample 4, the velocity determinations for which are given in Table 3, was taken from the center of the stack through a tube (A) of Jena glass 23 feet in length and one-half inch in diameter, with a small opening (O) through which the smoke was drawn. The sampling was begun August 23 at 10.55 A. M., and continued, with an hour's intermission, until the next day at 2.32 P. M. The total volume of the sample at 17° was 123.2 cubic feet, this being the meter reading, corrected for the error of the meter, and for the solubility of the gases in the absorbing liquid. Since in this case the opening (O) was so small that the sampling velocity did not need to be very great, it was decided to ascertain how much of the sample would deposit in the glass tube (A) (Figure 6). The tube (B) was omitted, but in its place, the tubes (C), (D) and (E) were fiilled with absorbent cotton. The velocity of the gas through the sampling tube itself was approximately one and one-half feet per second, the first fifteen feet of the tube from the opening having a temperature of 174.7° on the average, while in the remaining eight feet, the temperature fell gradually to about 25°.

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[1] To aid in the washing, the tube (A) may be cut into sections, and a glass rod with a rubber end used to loosen the adherent particles.

[2] The use of several large porcelain filters (six inches in diameter) has proved satisfactory in preliminary experimental work on the determination of the total solids. The first filters are covered with coarse, and the last with finely shredded asbestos. No liquid absorbent is used, but the tubes leading to the filters must be cleaned carefully. The weight is determined by direct weighing after drying. This method may be used where the more complex apparatus of our standard method is too cumbersome. Filter paper may be used for low velocities in cases where the smoke does not have a chemical action upon the paper.

The deposit in the tube was washed with water, and the water solution analyzed for arsenic, giving 0.009496 grams of arsenic trioxide per cubic foot, or 53,580 pounds per day of soluble arsenic trioxide for the portion of the sample which settled in the tube. The solution in the flasks was filtered, and the filtrate added to the water washings of the cotton. On analysis, this gave 0.001446 grams of arsenic trioxide to the cubic foot, or 8,200 pounds per day, which shows that 87.7 per cent. of the soluble arsenic was collected in the glass tube (A). The insoluble portions were analyzed together, and gave 6,000 pounds per day of water insoluble arsenic calculated as arsenic trioxide. This sample gave as a result, 61,780 pounds of water soluble arsenic trioxide; 6,000 pounds of water, insoluble; and a total of 67,780 pounds of arsenic trioxide per day as the amount sent out in the smoke.

In the case of Sample 2 (See Table 4 for the velocity determination), the sample was divided into two parts; the water soluble and the water insoluble. The sample was taken from a point four feet from the inner wall of the stack, beginning July 23, 1905, at 1 A. M., and stopping at 10.35 P. M. the same day. Of this time there were four hours during which the sampling apparatus was not running. The results of this test are shown in Table 7, which gives the results for the more impor-

TABLE 7.

APPROXIMATE AMOUNTS OF SUBSTANCES EXPELLED IN THE SMOKE, AS DETERMINED FROM SAMPLE 2.[1]

	Water Soluble.		Water Insoluble.		Total.	
Substance.	Grams per cu. ft.	Pounds per day.	Grams per cu. ft.	Pounds per day.	Grams per cu.ft.	Pounds per day.
Arsenic trioxide	0.01212	52,650	0.001428	6,204	0.01355	58,854
Antimony trioxide	0.000650	2,800	0 000321	1,400	0.000971	4,200
Copper	0.00071	3,100	0.00046	2,000	0.00117	5,100
Lead	trace		0.00110	4,800	0.00110	4,800
Zinc					0.0013	5,500
Iron and Aluminum Oxides	0.00318	13,800	0.00221	9,600	0.00539	25,400
Bismuth					0.00021	880

[1] Volume of smoke per day for Sample 2 = 2,007,000,000 cu. ft. under the conditions of the meter. Volume of sample (corrected) = 72.53 cu. ft.

tant metals. Where only the total is given, the soluble and insoluble portions were united before making the determination.

The analysis of Sample 3 (velocity of determination, Table 5) is given in the form of a table of the same kind (Table 8).

TABLE 8.

APPROXIMATE AMOUNTS OF SUBSTANCES EXPELLED IN THE SMOKE, AS DETERMINED FROM SAMPLE 3, JULY 27, 1905.

	Water Soluble.		Water Insoluble.		Total.	
Substance.	Grams per cu. ft.	Pounds per day.	Grams per cu. ft.	Pounds per day.	Grams per cu. ft.	Pounds per day.
Arsenic trioxide	0.00988	47,000	0.00089	4,210	0.01077	51,210
Antimony trioxide					0.00093	4,400
Copper	0.00058	2,700	0.00023	1,080	0.00081	3,780
Lead			0.00100	4,750	0.00100	4,750
Zinc	0.00137	6,480			0.00137	6,480
Iron and Aluminum Oxides	0.00109	5,280	0.00162	7,680	0.00271	12,960
Silica					0.00219	10,260
Manganese	0.000040	180			0.000040	180

Volume of Smoke per day under the conditions of the meter = 2,161,000,000 cu. ft. Volume of sample (corrected) = 72.40 cu. ft.

In obtaining the above results, standard analytical methods were used, the arsenic determinations being made, as a rule, in triplicate, using different methods. The arsenic and antimony were separated from the lead, bismuth, and copper, by the use of chemically pure sodium sulphide, using in each case a fresh solution. The arsenic was separated from the antimony by a fusion method, by distillation, or by precipitation of the pentasulphide in a strong hydrochloric acid solution, the last method being preferred. In this case the pentasulphide was first weighed in a platinum Gooch crucible, then dissolved in caustic potash, oxidized by chlorine, acidified with hydrochloric acid, the chlorine boiled off, and the arsenic finally precipitated in an ammoniacal solution as magnesium ammonium arsenate. The solution was then filtered through a platinum Gooch crucible, and the precipitate heated by a Bunsen flame, the platinum crucible being protected from too high a temperature by a large porcelain crucible in which it was placed. The antimony was precipitated as antimony trisulphide, filtered through a Gooch crucible, and the precipitate heated in a stream of carbon dioxide in a Paul's drying oven. The lead was determined as sulphate, and by electrolysis; the bismuth, separated by repeated precipitations with ammonium carbonate; and the copper determined by electrolysis.

Sulphur Dioxide. Five determinations of sulphur dioxide, made August 25, 1905, will be given here to show something of the amount of sulphur dioxide which is thrown off by the smelter. Other determinations were made at different times, but will not be reported, since there is some uncertainty due to a loss of a portion of the notes. The gas itself was drawn through tenth normal iodine solution, from ten to forty cubic centimeters being used for each test. The results were calculated from the formulas:

$$V_1 = \frac{V\,(B-w) \times 273}{760 \times (273 + t)} + 11.19 \qquad \text{where } B = 613.4,\; w = 14.4,\; t = 17'\text{C}$$

$$\%\ SO_2 = \frac{1119}{V_1}$$

The results of these determinations are shown in Table 9, where the probable value is calculated from the formula, $r = 0.6745\sqrt{\frac{v^2}{n-1}}$ where r is the variation of the probable value from the determined average.

TABLE 9.—PERCENTAGE OF SULPHUR DIOXIDE.

No.	Volume sample.	Vol = 10 cc. I.	V_1	Per cent. SO_2	v	v^2
1	2100 cc.	1050	790.2	1.417	— .076	.005776
2	900	900	679.0	1.648	+ .155	.024025
3	1020	1020	768.0	1.458	— 0.35	.001225
4	3815	953.7	718.2	1.558	+ .065	.004225
5	3225	1075	809.0	1.384	— .109	.011881

Average per cent. by volume of SO_2 = 1.493 ± .0732.

Gravimetric determinations of sulphuric acid were made on the remaining solutions, and the sulphuric acid determined by difference. The average percentage by volume was 0.114.

A summary of the volume determinations and analyses of the smoke, is given in Table 10, where all the results for volume are given as calculated to uniform temperatures and pressures. The results for sulphur dioxide are obtained by taking the average percentage, and calculating the amount for each volume as given for the separate volume determinations.

TABLE 10.—SUMMARY OF THE VOLUME DETERMINATIONS.

Sample.	Velocity ft. per sec.	Cu ft. per day at temp. of stack = 174.7° p = 612.2 mm.	Cu. ft. per day at temp. surrounding air = 17° C.	Cu. ft. per day standard conditions.	Tons Sulphur dioxide per day
3	46.43	3,098,000,000	2,007,500,000	1,523,000,000	2,038
2	50.04	3,337,000,000	2,161,000,000	1,641,000,000	2,195
5	59.24	3.951,000,000	2,561,000,000	1,942,000,000	2,597
4	55.80	3,721,000,000	2,411,000,000	1,828,000,000	2,443
Average	52.88	3,526,800,000	2,285,100,000	1,733,500,000	2,318

AVERAGE IN POUNDS PER DAY OF SUBSTANCES THROWN OFF IN THE SMOKE.

Arsenic trioxide	59,270
Antimony trioxide	4,320
Copper	4,340
Lead	4,775
Zinc	6,090
Oxides of Fe and Al	17,840
Bismuth	880
Manganese	180
Silica	10,260
Sulphur trioxide	447,600
Sulphur dioxide	4,636,000

These results show that while the great flue, previously described, may be fairly efficient in settling the copper from the smoke, still a considerable amount escapes, while the amount of arsenic given off is very great. The greater part of this arsenic is in the form of the trioxide, though the crystals are somewhat rounded. A small amount exists as the trisulphide, and in the form of complex minerals containing iron. No attempt was made to identify the latter, but, judging from the ore, there was undoubtedly some enargite present.

Samples of flue dust were taken from the big flue in August, 1905, beginning at the bottom of the stack, and sampling at approximately equal intervals to the bottom of the sixty foot flue, a distance of about 2,200 feet. The results of the analyses for copper and arsenic as given in Table 11, throw some light on the efficiency of the flue, especially when the results of the analyses of the smoke are also considered. The flue collects daily approximately fifty tons of dust, but it seems evident that the amount collected near the stack would be much less than that collected in the portion nearer the furnaces.

TABLE 11.—ANALYSES OF FLUE DUST.

Number.	Location.	Per cent. Cu.	Per cent. As_2O_3
1	Near foot of stack	4.64	26.06
2		5.23	22.00
3		5.85	16.40
4	Bottom of 120′ flue	5.89	12.62
5	Near top of narrow flue	6.33	10.32
6		7.37	8.85
7	Bottom of narrow flue	8.00	7.14

Dust collected from the outside of the glass sampling tube in the stack gave 25.7 per cent., and dust which dropped from the top of the stack, 25.63 per cent. of *soluble* arsenic calculated as trioxide.

The flue dust at the top of the big flue is roasted to produce commercial arsenic trioxide, but all of the rest is sent to the reverberatories and smelted for copper, so that the arsenic which it contains must in the end be eliminated in the smoke, excepting only that portion which goes into the reverberatory slag.

The amount of copper deposited is greatest at the bottom of the flue, just as would be expected, since the copper is not in a volatile state; but the amount of arsenic increases rapidly as the stack is approached. The flue evidently ends just where it is beginning to be very effective in the condensation and settling of the trioxide of arsenic, and the greater part of this substance passes out through the stack. However, even at the bottom of the sixty foot flue a considerable amount is deposited. It is evident that a large percentage of the oxide of arsenic which condenses to the solid state while in the flue, is carried along simply because it is so fine that it will not deposit at the rate the gas is moving, 11.4 feet (3.47 meters) per second. Most of the crystals which were obtained in the stack, were from 0.006 to 0.020 millimeters in diameter, but collected together in larger masses. After withdrawing each sample of smoke the sampling tube (A) (Figure 6) contained considerable loose dust which ran high in arsenic, and on the walls of the tube there was always some of the trioxide which had crystallized from a vapor. The sulphides of lead, bismuth, and arsenic were deposited in definite rings on the walls of this tube. The flue collects the greater part of the heavy metals, but allows the most of the white arsenic to pass as a finely divided solid, and as a gas.

The General Effects of the High Stack.—The change from low stacks to a very high one, has given an excellent opportunity to observe the difference in their effects. The result of the change has been to decrease the amount of arsenic deposited near the stack, and to spread it over a greater area. On account of the higher specific gravity of the smoke, it tends finally to fall to the earth, even though it may first be carried to a very great height, often striking the ground at distances of from one to four miles. As a general thing, the sulphur dioxide is more dilute when it reaches the ground than it was in the case of the lower stacks. However, there is often a greater amount of damage done in certain valleys which were previously protected by the mountains, but into which the smoke can now drop. The trees on certain high mountain sides are also acted upon more than before, in some cases showing a streak in the forest where the current of smoke passes, while below this the damage is less noticeable; but usually the gas finally descends into some valley. At times, in a high wind, the smoke will come to the ground at the base of the stack; and the leaves of shrubs in the valley about half a mile from the stack, and 1000 feet lower than its top, show a very high percentage of arsenic.

On the contrary, in still weather, the smoke sometimes rises very high, and seems to be carried away at a great elevation. It is certain, at least, that on level land, near the stack, the action of the sulphur dioxide is less intense than before, and as a result it is easier to raise trees and vegetables. In spite of these beneficial results the building of a high stack cannot always be recommended. Such a case was that of the Keswick smelter, where the smelter lay in a low, narrow valley. The short stacks threw out smoke which killed practically everything within a mile and a half on the low land. This district would have been of little use had a high stack been constructed, and the result would have been to spread the injurious action over an undamaged area, only to protect that which was already ruined.

In order to determine to what extent the smoke was diluted before striking the ground, one sample of air taken at a distance of two and one half miles was analyzed for arsenic, and gave three thousandths of a milligram of the oxide to a cubic foot. In this case we were in the rapidly passing clouds of dilute smoke only about one fourth of the time. Another analysis at the same distance gave one part of sulphur dioxide to thirteen thousand parts of air. Analysis of cloths, snow, wood, grass, and other substances showed considerable quantities of arsenic: most on surfaces turned upward, slightly less on vertical sides facing the smelter, and very little on vertical sides facing away from the smelter. The arsenic in the smoke as shown by the analyses, was, in the three cases, 91.8 per cent. 91.1 per cent., and 89.4 per cent. soluble in water; and the arsenic in two samples of grass was 92.6 per cent. and 83.6 per cent. soluble in the digestive fluids of the cow. As a rule, the arsenic in the grass is less soluble than that in the smoke, since the rains wash away the more soluble portions. The subject of the deposition of the arsenic will be treated in detail in the second article of this series.

The concentration of the sulphur dioxide in the air of a smelter district is much more variable than in the great cities during the winter. In neither case, however, is much known of the actual percentages present. While the amount present in a concentration of even a few hundredths of a per cent, may easily be determined by absorption in iodine or potassium permanganate, no method is at present known for the determination of the minute amounts of sulphur dioxide present in ordinary or even city air. The best that can be done at present is to approximate the total amount of sulphur gases in the air. A great deal of work has been done upon this subject recently in the smelter regions of the west using a solution of sodium bicarbonate or sodium carbonate as an absorbent. It should be emphasized that such alkaline liquids are wholly unsuitable as absorbents for sulphur dioxide, since even a ten per cent. potassium hydroxide solution does not completely absorb this gas.

In cities, sulphur dioxide is present in the greatest quantities during the winter, when it can have little action upon plant growth. In smelter regions, the amount of sulphur dioxide in the air depends more upon the winds and the humidity than upon the season of the year. The highest results for sulphur gases in city air were obtained by Oliver, who drew London air through dilute hydrogen peroxide. The amounts obtained were as follows:

	Per cubic meter.				Parts per million.
Cloudy weather	1.9 mg, SO_3	=	1,52 mg. SO_2	=	1.17 SO_2
Light fog	2.9	=	2.52	=	1.95
Heavy fog	6.0	=	4.80	=	3.71
Yellow fog	7.2	=	5.76	=	4.45
Black fog	14.1	=	11.28	=	8.73

A comprehensive treatment of this subject is given by Max Rubner.[1] The determination of the amount of sulphur dioxide in the smoke stream is much more simple, since the concentration of the gas is considerable. The principal difficulty where high stacks are in use is that the smoke stream shifts so rapidly that it is usually impossible to follow it. The best time for such a determination is at night, when the smoke often settles in a cloud in the valley.

Many interesting problems have arisen in this work which could not be solved on account of lack of time. It is possible that the flue dust, as assorted by the flues and chambers, would supply a good field for work on the rare elements. An analysis made several years ago gave 0.011 per cent. vanadium, 0.027 per cent. selenium, and 0.016 per cent. tellurium; while a qualitative examination for the ordinary elements showed, in addition, the presence of silver, lead, bismuth, copper, arsenic, iron, aluminium, manganese, zinc, barium, calcium, magnesium, sodium, ammonium, silica, water, sulphuric acid, chlorides, sulphides, sulphites, sulphates and a trace of organic matter. Other elements might have been present in traces. The dust from the flue near the stack, or in the stack itself, contains a considerable amount of concentrated sulphuric acid, while that from near the furnaces contains much less. To this latter, together with the arsenic with which it is associated, is probably due much of the spotting of leaves which is so common in smelter regions. This action of the flue dust is of far less importance than that of the sulphur dioxide[2] in affecting the growth of plants, in spite of some recent opinions to the contrary; but the arsenic of the dust may affect to a greater degree the value of the grasses, since it renders them poisonous.

In conclusion, we wish to express our special indebtedness to Dr. John Maxson Stillman, who has helped us very greatly in all of this work. We wish also to thank Captain D. W. Taylor for the design of the Pitot tube, Professor Robert Sibley for checking the calculations, and Professors W. R. Eckart, Jr., W. F. Durand, and Albert W. Smith, for aid, and for suggestions as to the determination of velocity.

THE UNIVERSITY OF MONTANA AND STANFORD UNIVERSITY, April 22, 1907.

[1] Rubner, Archiv. für Hygiene, LVII, 323-378; LIX, 91-149.

[2] For a comprehensive bibliography on the subject of damage by smelter smoke see: Haselhoff und Lindau, Die Beschädigung der Vegetation durch Rauch, Leipzig, 1903; Schroeder, J. v., u Reuss, C., Die Beschädigung der Vegetation durch Rauch und die Oberharzer Hüttenrauchschäden, Berlin, 1883.

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PAPERS ON SMELTER SMOKE.

[SECOND PAPER.]

ARSENIC IN VEGETATION EXPOSED TO SMELTER SMOKE.[1]

BY R. E. SWAIN AND W. D. HARKINS.

Received January 28, 1908.

In a previous paper[2] there were presented the results of a study of the smoke emanating from a copper smelter now in operation near Anaconda, Montana. It was estimated that at the time the examination was made this plant was discharging daily from its main chimney an average of 59,270 pounds (26,880 kilograms) of arsenic trioxide, along with notable quantities of copper, antimony, lead, zinc, and other substances. The smelter is situated at the base of a ridge which descends steeply from Mt. Haggin, a perennially snow-capped peak rising near the main crest of the Rocky Mountains. On one side of this ridge is the valley of Warm Springs Creek in which the city of Anaconda is situated, and on the other side is Mill Valley, each typical of a number of narrow valleys and ravines leading down from the main range into a broad basin thirty-five miles long and four to six miles wide, the Deer Lodge Valley. The present paper will deal with the distribution of certain of the more notable constituents of the smoke, particularly arsenic, over the district in the vicinity of the smelter. This is a region of variable winds which often blow with great velocity, so the section affected by the solid or gaseous components of the smoke is not confined to a narrow tract nor to any closely circumscribed area. There are prevailing wind directions for each season of the year, but these are not so constant as to restrict the action in any considerable degree. Pouring out of the stack a thousand feet above the valley floor, the smoke stream can be traced as far as the eye can reach in that normally clear atmosphere, trailing down the valley for thirty miles toward Garrison, or often eastward in the direction of Butte, or sweeping over into Mill Valley and filling the narrow ravines which lead down from the Continental Divide, fourteen miles to the south. In spite of the height at which it is discharged the smoke may be seen very frequently to strike the valley within less than a mile from the base of the stack, while on quiet days it may rise to a considerable height and hang as a haze over the valley.

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[1] The work on this paper was begun in 1902 by W. D. Harkins, and was presented in abstract at the New York meeting of the American Chemical Society, December, 1906.

[2] THIS JOURNAL, 29, 970.

The basis of the work herein described has been the vegetation of the Deer Lodge Valley and adjacent territory, and especially the hay and wild grasses, for the primary incentive to the investigation, part of which preceded the examination of the smoke itself, was the claim on the part of the farmers residing in the vicinity of the smelter that they were suffering abnormal losses of live-stock, which they attributed to smelter fumes. The first appearance of the peculiar symptoms of disease in the stock were noticed only a few months after the smelter began to operate; the quick recovery of the milder cases upon removing them to distant pastures, and the recurrence of the disorder on their return; and the fact that the greatest disturbance was observed in those sections over which the smoke drifted most frequently, suggested that the trouble was a local one and in some way connected with the smelter.

In all cases the samples analyzed were collected by one of us or by both of us together, either in stoppered bottles or in heavy glazed jute sampling bags. With very few exceptions the results obtained are from air-dried samples, this being deemed a more reasonable and practical basis to which to refer the analyses than the more complete drying at 100°.

From each of these samples a weighed quantity (30–200 grams) was taken for analysis, placed in a large casserole covered with a watch glass and concentrated nitric acid allowed to stream over it from a pipette. Destruction of the tissue begins at once without the application of heat, and in the case of samples with many leaves which present extensive surfaces for action, the mass may ignite[1] and burn, if not carefully watched during the first stage of the decomposition. Excessive action must be checked promptly by floating the vessel in cold water or, if that is insufficient, by diluting the acid with water. By stirring it occasionally with a glass rod the sample is soon reduced to a thick, yellow, semi-liquid mass after which heat may be applied to the casserole until the most of the acid is expelled. Five to 8 cc. of concentrated sulphuric acid are then added, drop by drop. A rapid decomposition of nitro-compounds fol-

[1] If a large amount of acid is added there is no danger of ignition even if concentrated nitric acid is used.

lows and thereafter the mass is reduced to a charred and crisp condition by heating in an air bath to a temperature not exceeding 180°.[1] If the destruction of the tissue is not perfect enough after the addition of the sulphuric acid, successive small portions of nitric acid may be added during the subsequent heating, taking the precaution to cool the casserole to 100° or less before each addition. This method, which is essentially an application to plant tissue of the Chittenden-Donaldson method for the destruction of animal tissue, yields a final residue capable of easy extraction with acidified water. The extract thus obtained was filtered into a graduated flask and an aliquot part taken for analysis.

In all but a few cases the arsenic was estimated by applying the Marsh-Berzelius method and weighing the mirrors which resulted. In no case in which results are given was an estimate based upon comparative mirrors.

Copper was determined by evaporating another portion of the solution to dryness in a porcelain dish, igniting to destroy all organic matter, and after dissolving the residue in dilute nitric acid, precipitating the copper electrolytically. The following table gives the results of the analysis of vegetable tissue collected in the Anaconda region:

TABLE I.—ARSENIC AND COPPER IN GRASS AND HAY.

Number.	Sample.	Month.	Distance and direction.	Parts per million.[2]	
				As_2O_3.	Copper.
		1902			
1	G[3]	Nov.	0.25 E	1551	1800
2	G	Nov.	3.0 W	166	871
3	G	Nov.	4.0 W	88	708
4	H	Nov.	1.5 S	283	...
5	H	Nov.	3.0 W	36	216
		1903			
6	G	Oct.	4.0 E	10	128
6*a*	G	Oct.	2.0 S	11	...
6*b*	G	Oct.	4.0 SE	13	...
7	H	Oct.	5.0 SE	13	...
8	G	Nov.	15.0 NNE	52	164
9	M	Nov.	15.0 NNE	405	237
		1905			
10	G	Jan.	3.0 N	122	...
11	G	Jan.	5.0 E	100	563
12	G	Jan.	5.0 ESE	90	
13	G	Jan.	2.0 SSE	79	176

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[1] Another method used by one of the writers will be described in a subsequent paper.

[2] Parts per million are equivalent to ten-thousandths of 1 per cent., and multiplied by 0.7 give the number of grains in 100 pounds of substance.

[3] H denotes a sample of hay taken from the stack; G, a sample of grass cut from the field; L, leaves of trees; B, bark of trees; C, leaves of the cedar; and V, leaves of the lily-of-the-valley.

TABLE I (*Continued*).

Number.	Sample.	Month.	Distance and direction.		Parts per million.	
					As_2O_3.	Copper.
14	G	Jan.	4.0	SE	50	80
15	H	Jan.	2.0	SSE	23	11
16	G	Jan.	2.5	SW	87	81
17	G	Jan.	4.0	ESE	68	150
18	H	Jan.	3.0	SE	8	51
19	G	Jan.	6.0	NE	170	226
20	H	Jan.	4.2	NE	85	.
21	H	Jan.	3.0	NE	96	326
22	G	Feb.	3.0	N	77	112
23	G	Feb.	2.0	N	220	119
24	G	Feb.	4.5	N	217	407
25	H	Feb.	4.0	SE	22	...
26	H	Feb.	4.0	SE	21	...
27	H	Feb.	5.0	ESE	50	46
28	G	Feb.	6.0	N	30	112
29	G	Feb.	5.0	N	263	470
30	G	May	35.0	N	35	...
31	H	June	4.5	N	89	161
32	G	June	6.0	N	67	...
33	H	June	12.0	NNE	35	190
34	H	June	2.0	W	15	...
35	H	June	14.0	NNE	34	221
36	G	Sept.	6.0	N	61	...
37	L	Sept.	0.5	W	427	...
		1906				
38	G	Feb.	5.0	SE	140	
39	G	Feb.	5.5	N	180	
40	H	June	3.0	W	14	
41	G	June	4.0	W	99	
42	H	June	3.0	E	107	
43	H	June	4.0	E	18	
44	G	July	4.2	N	12	
45	G	July	8.0	NNE	111	
46	G	July	5.0	W	38	
47	G	July	3.0	SE	21	
48	G	July	1.5	SW	157	
49	G	July	2.0	S	10	
50	G	July	2.0	SW	359	
51	G	July	1.5	SW	460	
52	G	July	1.7	SW	293	
53	V	July	1.7	SW	583	
54	B	July	1.5	SW	350	
55	B	July	1.7	SW	376	
56	G	July	6.0	N	18	
57	C	July	2.0	SW	508	
58	G	July	0.7	SW	431	
59	H	Aug.	6.0	E	31	
60	B	Aug.	1.5	SW	300	
61	L	Aug.	1.7	SW	683	

TABLE I (*Continued*).

Number.	Sample.	Month.	Distance and direction.		Parts per million. As_2O_3.
62	G	Aug.	1.7	SW	482
63	G	Sept.	2.5	NW	81
64	G	Sept.	2.5	SW	100
65	G	Sept.	6.0	N	33
66	G	Sept.	4.2	N	34
67	G	Sept.	1.0	N	101
68	G	Sept.	1.0	E	236
69	G	Oct.	10.0	SW	64
70	G	Oct.	13.0	SW	38
71	G	Oct.	35.0	N	29
72	G	Oct.	34.0	N	21
73	G	Nov.	4.2	NNE	121
74	G	Nov.	6.0	NNE	73
75	G	Nov.	1.5	E	705
		1907			
76	G	Jan.	1.0	NE	265
77	G	Jan.	2.0	SE	97
78	G	Jan.	3.0	SSE	51
79	G	Jan.	4.0	SE	86
80	G	Jan.	4.0	SE	76
81	G	Jan.	6.0	SSE	47
82	G	Jan.	6.5	SE	98
83	G	Jan.	8.0	SE	79
84	G	Jan.	100.0	NW	00
85	G	Jan.	75.0	W	00
86	G	Oct.	100.0	NW	00

A few of the above samples were analyzed by each of us, using the same balance sensitive to 0.005 mg., but otherwise independently, and the mean of the results obtained taken for the table above. The complete data for each joint determination are given as follows:

TABLE II.

No.	Sample.	Per cent. As_2O_3. H.	Per cent. As_2O_3. S.	Difference. Per cent.
11	Grass	0.0103	0.0097	0.0006
16	Grass	0.0089	0.0085	0.0004
19	Grass	0.0169	0.0170	0.0001
20–31	Hay	0.0089	0.0085	0.0004
22	Grass	0.0079	0.0075	0.0004
23	Grass	0.0219	0.0220	0.0001
29	Grass	0.0264	0.0261	0.0003
33–35	Hay	0.0034	0.0035	0.0001

In all but two cases of those cited above the results given are merely duplicate determinations made on a single sample, but samples 20 and 31 and samples 33 and 35 were instances where each of us took a sample from a stack independently of the other and conducted a separate determination.

The first samples taken from this district were collected in November, 1902, but the record of all except nine of the results of the analyses made on this material and that of the following year was accidentally destroyed. The smelter started early in 1902 and continued without interruption throughout that year, so the results for grass represent a deposition of arsenic extending over a period of six months, while the hay, cut in July, was exposed less than three months. Samples 2 and 5 were taken from the same farm, but one was left exposed in the field during the whole period while the other was removed and stacked as hay. The difference here shown in the two values, 166 and 36, respectively, is fairly representative of a condition which will be found to prevail with notable uniformity throughout the analyses. An interesting exception is found in the data for 1903, where samples 6 and 7 show quantities which are not only relatively very low, but nearly equal. During 1902 and a part of the following year the smoke from the smelter was delivered from four smaller stacks which were erected near the center of the plant. But in June, 1903, the smelter was shut down until late in September in order to permit certain modifications to be made, chief among them being the final work of construction upon the present high stack and extensive settling flue. At the time these samples were collected, one from a haystack and the other of grass from the open field, the smelter had barely begun operations after the summer's inactivity, so that the two samples had been exposed to smoke only during the period of growth until the time of the closing down of the smelter in June, and both were exposed equally long. Sample 8 shows the result of an added exposure of over a month during the dry season of the year. The moss sample from the same locality gave a remarkable result which is to be explained only on the assumption that owing to its peculiar matted growth the moss may have collected the arsenic which fell upon it like a natural filter, and held on to it from the previous year. During the year 1904 no collections were made, though the hay samples taken in the early part of 1905 were from the 1904 crop. The average amount of arsenic in these hay samples collected up to May, 1905, is 41.9 parts per million, while the average of the results for grass is 120.4.

For the year 1905 a noteworthy sample is that of grass (No. 30) from Garrison, thirty-five miles north of the smelter, which carried 35 parts of arsenic trioxide per million. Two samples (Nos. 71 and 72) collected in October of the following year from the same locality carried 29 and 21 parts, respectively, per million. The former sample was old grass collected in May, at which time the grass from the preceding year usually attains its maximum content of arsenic.

It must be admitted that, whatever the amount of arsenic discharged daily with the smoke, we have, without further evidence, no satisfactory measure of its distribution. If arsenic and copper and other toxic constituents of smelter smoke were not to be found in the soil, their appearance in the vegetaton of the smoke zone could be attributed at once to atmospheric deposition. But it may be claimed that the arsenic and copper found in these samples are not deposited from the smoke stream, but absorbed from the soil itself. It is a fact that growing plants may absorb small amounts of copper from the soil, and a review of the literature would seem to leave no doubt that the same is true, in a very slight degree, for arsenic.

Voelcker[1] experimented with grass grown on soils to which arsenical superphosphate had been added, and Hehner, who made the analyses for him, found on an average 0.0045 grain of arsenic per pound of straw (0.7 part per million). Swedes under the same conditions gave no arsenic in the bulbs, and in one case only 0.02 grain per pound of dried tissue (2.8 parts per million) in the leaves and stems. Barley straw grown on soil manured heavily with superphosphate containing 0.5 per cent. arsenic trioxide carried 0.007 grain per pound (1 part per million) while the leaves of swedes and mangels grown on ordinary soils containing about 0.0002 per cent. of arsenic trioxide were found to contain 0.002–0.004 grain of arsenic per pound (0.3 to 0.6 part per million). Angell[2] analyzed a large variety of cereals and table vegetables which were grown on soil to which superphosphate carrying 0.5 per cent. of As_2O_3 was added. Of thirty-two samples examined twenty-two showed not a trace of arsenic while the rest are reported as containing slight traces. Since, however, only an acid extract of the plant in dilute hydrochloric acid was made, with no effort to destroy organic matter before adding it to the Marsh generator, and since only fifteen minutes were allowed for the arsenic mirror to appear, the results are open to very serious question. Gautier[3] found arsenic in many vegetable foodstuffs; in wheat (0.000,007 per cent.), bread (0.0000071 per cent.), and in potatoes (0.000,0112 per cent.), but not a trace in cabbage and beans. He also claims to have found it in marine and fresh water algae.

Copper in traces has been shown repeatedly to be present in plants grown on coppery soils. In fact the occasional presence of copper in plants has been admitted for nearly a century.[4] Verdrödi[5] found notable amounts of copper in buckwheat (0.87 per cent. CuO), maize (0.06–0.39 per cent.) and other cereals. These results, however, have been criticized by Lehmann,[1] who points out that they are ten times those obtained by Tscherch from soils very rich in copper, and justly criticizes the method adopted by Verdrödi for the estimation of copper, *viz.*, ashing the plant, extracting the residue with nitric and hydrochloric acids, precipitating with hydrogen sulphide, and without further treatment weighing the precipitate as copper sulphide. Lehmann's own results, however, show that minute quantities of copper may be present in certain plants which subsist on a soil containing copper salts.

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[1] *Report Royal Arsenical Commission*, Vol. II, p. 174.

[2] *Ibid.*, p. 10.

[3] Gautier, *Compt. rend.*, **139**, 101 (1904).

[4] See Meissner-Schweigg, Journal, **17**, 340 (1816); Phillips, *Ann. chim. phys.* [2], **19**, 76 (1821).

[5] Verdrödi, *Chem. Z.*, **17**, 1932 (1894); and **20**, 399 (1896).

There are good reasons for believing that the values given for arsenic and copper in the previous table are not due to absorption from the soil. Plants do not absorb so much arsenic or copper as is there shown. The writers have grown cereals on several soil samples which were collected in the Deer Lodge Valley. These were taken outside the range of the smelter smoke and planted to barley and timothy. In no case have they found more than 0.0002 per cent. of arsenic trioxide in the matured plants, where values as high as 0.0263 per cent. had been obtained from grass grown on the same soil five miles from the smelter. Moreover, above everything else the length of time the plant is exposed to the free atmosphere in the smelting district is the determining factor in connection with its arsenic content. A few cases illustrating this have already been cited in connection with some of the earlier results, and many others could be selected. Nos. 53 and 61, samples of wild lily-of-the-valley, were collected by one of us from the same spot about one and three-quarter miles from the smokestack and in a section over which the smoke blows much of the time in the summer months. The first one was cut July 3rd and the other August 14th, or six weeks later. During this time the arsenic content of the plants increased from 583 to 682 parts per million. At the same time these were taken a kind of wild grass (*agripirons divergens*) growing at the same place was sampled. These are designated as Nos. 49 and 62. When the first of these was collected the grass was already dead, so the increase in arsenic trioxide from 293 to 482 parts per million cannot be ascribed to processes of absorption from the soil. Nos. 44, 66 and 73 are meadow grass samples taken from the same field in the months of July, September and November, respectively. The July sample, covering the period of most rapid growth and most frequent rainfall, carried 12 parts of arsenic trioxide per million. The September sample more than covered the rest of the growing period and carried 34 parts, while the November sample carried 121 parts per million, thus collecting an added 87 parts after all growth had ceased.

A striking proof that the arsenic is deposited from the smoke was found by a study of the wind currents. The Mill Valley district southwest of the smelter is the one toward which the smoke blows most during the early summer, while late in August the air currents begin to go northward down the Deer Lodge Valley, and from this time until the snow covers the ground the greater part of the smoke blows in this direction. The analyses show that the grass of Mill Valley contains more arsenic than any other district during the early summer. Thus samples 48, 50, 51, 52, 53 and 58, which were gathered in July, 1906, contained respectively 157, 359, 460, 293, 583 and 431 parts of arsenic trioxide per million. North of the smelter, sample 12, taken in July 1906, from the Bliss ranch, contained 18 parts, one taken in September 33 parts, and one taken in November 73 parts of the trioxide per million. In 1905 the Bliss grass in June contained 67 parts, in September 61 parts, and in February, 1906 (grass of the season of 1905) it contained 180 parts per million. Hay from the same ranch cut in August, 1904, contained only 30 parts to the million, while by the next April the grass in the same field had increased its arsenic content to 263 parts. During 1906 the Para ranch gave 12 parts in July, 34 parts in September, and 121 parts in November. There is, of course, some objection to a comparison of the grass with the hay, since a certain portion of the arsenic of the latter is shaken off by the cutting and stacking. Even with the grass it is difficult to obtain the original arsenic content, since the sample must be cut, put into containers, and transported to the laboratory.

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[1] *Arch. Hyg.*, 24, 3; and 27, 1 (1896).

These results show very plainly that the greatest accumulation of arsenic generally occurs after the period of growth is ended and the plant is dead. There is little doubt that the rains during the early summer wash much of the arsenical deposit from the vegetation, while in winter the grass is protected by snow. The most favorable time then for the arsenic to accumulate on the tissue is during the late summer and fall; and during that period, in fact when absorption through the roots is out of the question, since when the grass is dead the accumulation is most rapid.

That this is deposited arsenic rather than absorbed arsenic is evidenced further by the fact that by shaking dry hay or grass grown in the vicinity of the smelter a finely divided dark-gray powder, running notably higher in arsenic than the tissue from which it came, is obtained. Various samples of this dust were collected by shaking the hay or grass on a fork over a glazed cloth and separating leaves and fragments of the tissue by means of an 80-mesh sieve. This dust accumulates in quantity on the floors and rafters of hay lofts and in the mangers of feeding barns where it can be swept up in large amounts. Several samples of dust were also obtained from parts of threshing machines and analyzed for arsenic. Complaints are often made by men working on these machines that the thresher dust from grain in the smoke zone irritates the skin and the mucous membrane of the eyes and nasal passages.

TABLE III.—ARSENIC IN DUST FROM HAY AND GRAIN.

No.	Year.	Month.	Sample.	Direction from smelter.	Distance from smelter.	As_2O_3. Per cent.	As_2O_3. Parts per million.	CuO. Per cent.	Farm.
1	1905	June	H.[1] Dust	N. E.	4.5	0.0987	987	0.5320	Para
2	1905	June	"	"	4.5	0.0969	969	0.5600	"
3	1905	Apr.	"	"	4	0.4380	4380	0.7430	Staffanson
4	1905	Apr.	"	"	4	0.5140	5140	0.7970	"
5	1905	Oct.	T.[2] Dust			0.0887	887		Bowman
6	1905	Oct.	"			0.0594	594		Perkins
7	1905	Oct.	"			0.0448	448		Watts
8	1905	Oct.	"			0.0410	410		Day
9	1905	Oct.	"			0.0941	941		Jones
10	1906	July	H. Dust	E.	1.5	0.3526	3526		Lappin
11	1906	Nov.	"	S. E.	2	0.9190	9190		Allen

These values are uniformly high, the richest of the hay dust samples exceeding any of those for the plant tissues many times over. The thresher dust samples run lower, due in part at least to the fact that the conditions under which that dust was deposited are more apt to cause a loss in arsenic and a concentration of the heavier silicious dusts. The samples of hay dust from the Para farm were collected from the stack from which hay samples 20 and 31 were taken. The hay averaged 87 parts of arsenic trioxide per million, while the dust shaken from it averaged 978 parts. The dust from the Staffanson hay contained 7700 parts of arsenic trioxide per million, while the hay itself carried 261 parts. In the case of Lappin's hay the dust carried 9190 parts and the hay 50 parts per million. Such results indicate clearly that the arsenic is deposited on the surface of the plant and is not distributed throughout the tissue.

A contention which might be raised is that this dust is soil which has been blown upon the hay, or which adhered to it during the process of curing in the field. Some representative analyses of soil taken to a depth of three inches are given in the following table:

TABLE IV.—ARSENIC IN SOILS.

Farm.	Distance.	Per cent. As_2O_3.
Staton	2 miles S.	0.0019
Callan	3 " S. W.	0.0029
Para	4.5 " N. N. E.	0.0043
Bliss	5.5 " "	0.0061
Staffanson	3 " "	0.0107

The Para hay dust then carried 22.7 times as much arsenious oxide as did the soil. The Lappin hay dust carried 483 times as much as the soil sample from the adjoining Staton farm; and the Staffanson hay dust contained 72 times as much arsenic as the soil upon which it grew. It is

[1] H = Hay.

[2] T = Thresher.

extremely unlikely that dust from the soil is any large contributor to the quantities of arsenic found in the hay dust. Rather would it appear more reasonable to assume that in so far as the soil is present it is a diluent which diminishes the percentage of arsenic. Originally the soil of this district does not seem to have been arsenical. The top three inches of uncultivated soil will usually afford small quantities of arsenic which rapidly vanish at greater depths. A sample of top soil taken from underneath a well built log house erected long before smelting operations began in that valley carried only a trace of arsenic, while soil from an adjoining field was found to contain 0.0107 per cent. in the top three inches. Soil which had never been plowed contained no arsenic whatever at depths of from twelve to fifteen inches, so the arsenic present in the top soil would seem to be due wholly to the smelter emanations.

Samples of snow were scraped from the surface at a time when the ground for miles was covered with a sheet which had not yet been disturbed by the wind. Considerable amounts of soluble arsenic were found, the arsenic being dissolved in the water formed when the snow melted. The appended table gives the analytical results obtained:

TABLE V.—ARSENIC IN SNOW.

Date, 1906.	Farm.	Distance and direction.	Weight of snow grams.	Sq. ft. surface area.	Time exposed.	As_2O_3 per sq. ft.	Per cent. of dust.
2–5	Para	5 miles N.	925	6.228	17 days	0.00306	0.1130
2–5	Williams	4 " N.	955	12.6	17 days	0.00026	0.1690
2–5	Bliss	5.5 " N.	...	...	17 days	0.00040	0.2810
3–18	Callen	3 " S. W.	808	13.45	3 days	0.00057	......
3–18	Bliss	5.5 " N.	604	6.72	3 days	0.00058	......

The figures in the column "Per cent. of dust" include the percentage of soluble arsenic calculated as if it were a component of the water-insoluble dust.

Early in the fall of 1905 vaselined cloths, each presenting a surface of three to eight square feet, were exposed at several points near the smelter. One was fastened to each side of a board tablet, somewhat larger than the cloth, which was set up on poles about twelve feet above the ground and broadside to the direction of the smoke stream at that place. Thus one vaselined cloth faced the smelter and the other faced in the opposite direction. In one case (No. 2) a cloth was stretched horizontally above the other two with its vaselined surface upward. Samples 1 and 2 were set up September 5th and taken down November 21, 1905. No. 3 was set up October 1st and taken down March 18th, but the vaselined surface was frozen hard and smooth for most of the winter and its efficiency as a collecting medium thus greatly decreased. The following data were obtained from this experiment:

TABLE VI.—ARSENIC IN VASELINED CLOTHS.

					As_2O_3 per sq. ft. of cloth.		
No.	Farm.	Direction from smelter.	Distance from smelter.	No. days exposed.	Facing upward, gram.	Facing smelter, gram.	Facing away, gram.
1	Bliss	N.	5.5	77	...	0.00052	0.00024
2	Para	N.	5.0	77	0.01194	0.00700	0.00083
3	Staton	S. E.	5.0	169	...	0.00327	0.00051

The results admit of only one interpretation, which is that the smelter smoke is the source of the arsenic found in such excessive amounts in the vegetation of the region about Anaconda. The question of whether this is a condition for which there is no remedy is difficult to answer. It is doubtful whether the present limited water supply would permit of the installation of wash towers, and the large amount of sulphur trioxide in the smoke would be destructive to a bag-house system. With its present high temperature and velocity the smoke must carry most of the arsenic out of the stack. In spite of the use of dry filters and wash towers and a consequent low velocity of the smoke, in an effort to meet the requirements of the amended Alkali Acts of 1892, the average escape of arsenic trioxide from the chimneys of arsenic plants in England for the past five years has been 0.0028 gram (0.041 grain) per cubic foot.[1]

In the thirtieth annual report[2] the Chief Inspector under the Alkali Acts wrote: "The inspection of these works (*i. e.*, arsenic works) had been much called for by residents in the district where they are found, and the necessity for the adoption of remedial measures was shown by the frequent litigation brought about by the alleged destruction of cattle through eating grass said to be poisoned by the arsenic too freely distributed through the air from the chimneys up which it had been carried by the draught. The arsenic driven off by the heat of the roasting furnace was caught and retained as far as possible, in long flues, culverts, and settling chambers, but although these were often of great extent, reaching in one place, a length of 2895 feet, or more than half a mile, and having a capacity of 60,795 cubic feet, yet arsenic was always liable to pass away. In one case a test of the chimney gases showed the presence of as much as 7.40 grains of arsenic trioxide in a cubic foot of gases passing into the air, and small flakes of it were seen falling continually in a mild snow-shower." The average escape of arsenic trioxide per cubic foot of chimney gases from plants provided with wash-towers, or with dry filters made by packing large chambers with brushwood, for each year since 1896 was as follows:

1896	0.080 grain
1897	0.086 "
1898	0.098 "

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[1] Annual Reports Chief Inspector under Alkali Acts 1902–6.

[2] 30th Annual Report under Alkali Acts (1893), p. 91.

1899	0.074 gram
1900	0.094 "
1901	0.083 "
1902	0.049 "
1903	0.039 "
1904	0.053 "
1905	0.036 "
1906	0.030 "

These results attest the difficulty of removing all the arsenic from chimney gases even where, as in many of the plants referred to above, the furnace gases are cooled by wash-towers and the velocity of the smoke is reduced by extensive settling chambers. The smoke proceeding from the smelter at Anaconda on the basis of results presented in the first paper carries about 0.200 grain per cubic foot, a considerable velocity even in the settling chambers and a chimney temperature of 180° both interfering strongly with the deposition of the arsenic. The quantity which is given off under the present smelting conditions is not likely to be reduced except by the use of a less highly arsenical ore. As the ore supply for the Anaconda plant in drawn entirely from the mines of the Butte district and the arsenic content of these ores seems to be constantly increasing as greater depths are reached, the prospect of finding a ready solution of the problem is not encouraging. The great value of the products lost in the smoke, as shown by the first paper of this series, should encourage smelter companies to conduct extensive experiments with a view to the mitigation of this evil.

TABLE VI.[1]

No.	Collected.	Sample.	Source.	As_2O_3. Per cent.	As_2O_3. Parts per million.
1	July 12, 1907	Grass	Everett, 300 ft. S.E. from smelter..	1.3000	13,000
2	July 12, 1907	Grass	Everett, ¼ mile S. E. from smelter.	0.9400	9,400
3	July 12, 1907	Poplar leaves	Everett, 50 ft. W. from smelter....	4.4000	44,000
4	July 12, 1907	Grass	Everett, 50 ft. W. from smelter....	0.2300	2,300
5	July 12, 1907	Grass	Everett, 100 ft. N. from smelter...	0.2300	2,300
6	July 12, 1907	Grass	Everett, ¼ mile N. from smelter...	0.0420	420
7	Aug. 11, 1906	Sunflower leaves, ¼ mile from Murray smelter, Utah		0.1072	1072
8	Aug. 11, 1906	Grass, ½ mile from Highland Boy smelter, Utah...		0.0062	62
9	Aug. 12, 1906	Alfalfa, 1 mile from Highland Boy smelter, Utah.		0.0038	38
10	Aug. 12, 1906	Grass, 2 mile from Bingham smelters, Utah......		0.0021	21
11	Aug. 12, 1906	Grass, 1 mile from Bingham smelters, Utah......		0.0045	45
12	Aug. 12, 1906	Milkweed, 3 miles from Highland Boy smelter, Utah		0.0027	27

Incidental to this work in connection with the smelter at Anaconda samples of plant tissue have been collected from two other prominent smelting centers, from Everett, Washington, about thirty miles north of Seattle, and from the region a few miles south of Salt Lake City, Utah, where several large smelters are in operation.[1] At both of these places complaints of injury to live stock have arisen from time to time. Only a few of these samples have been analyzed with the above results.

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[1] A large number of grass samples from other smelter districts have been analyzed since the completion of this paper. Many of these contain arsenic in large quantities.

The writers wish to express their indebtedness to Dr. John Maxson Stillman for suggestions in regard to this work.

THE UNIVERSITY OF MONTANA, MISSOULA, MONTANA, AND STANFORD UNIVERSITY, CALIFORNIA,
December 28, 1907.

THE CHRONIC ARSENICAL POISONING OF HERBIVOROUS ANIMALS.[2]

(PAPERS ON SMELTER SMOKE, THIRD PAPER.)

BY W. D. HARKINS AND R. E. SWAIN.

Received April 1, 1908.

The two outbreaks of supposed arsenical poisoning which have led to the most investigation from a scientific standpoint, are the one in Manchester, England, in the year 1900, and that in the district surrounding Anaconda, Montana, during the year 1902-1903. The former was confined to human beings, the latter almost entirely to cows, horses, and sheep. As yet very few data have been obtained to show whether or not the effects of the arsenic in the latter case extended to the human beings who resided in the district.

During the latter part of November, 1902, it was the fortune of one of us to travel over about one hundred square miles of the territory surrounding the new Washoe smelter at Anaconda. At that time the carcasses of several hundred animals that had recently died lay scattered over various ranches of the valley, and one ranch was visited where approximately sixty carcasses, mostly horses, were seen in a group in one corner of the field. A very large number of the animals were dissected, and practically all of them gave evidence of arsenical poisoning, either acute or chronic.

As has been explained more in detail in a former paper, what was called the "Old Works" had been in operation for many years on the north side of the valley of Warm Springs Creek, in which the city of Anaconda is located. In January, 1902, smelting operations were transferred to the "New Works," which are located on the south side of the same valley, on a ridge extending down from the foot-hills. This ridge projects into the Deer

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[1] See Ebaugh, Gases *vs.* Solids, THIS JOURNAL, 29, 951, 970 (1907).

[2] At the New York meeting of the American Chemical Society, December, 1906, W. D. Harkins presented a similar paper including only his own work. The first paper of this series deals with the amount and character of the smoke given off by the smelter, and the second treats of the arsenic content of the vegetation.

Lodge Valley in such a way that much more of the smoke from the smelter was blown across or into the valley than during former years.

Although the smelter was in operation during the whole year, few cases of serious sickness among live stock were noticed until September, from which time the number of deaths increased rapidly until November, when a maximum was reached. This is easily understood when the facts of the case are considered as presented in the second paper of this series.[1] The fresh grass of the spring has little time to accummulate arsenic from the air, and the summer is a period of rapid growth and frequent rains; in the autumn comes a dry period during which there is no plant growth, so this is the most favorable period for a rapid increase in the amount of solid substances adhering to the leaves and stems of the plant. During this dry period, the farmers were forced to drive or ship a great number of animals from the district, and those remaining were stabled and fed upon hay. The owners had found from their experience with the symptoms exhibited by the animals, that the disease was greatly moderated by changing the diet from grass to hay. This was explained by the much smaller amounts of arsenic found in the latter.[2]

In 1903 the smelter company had built the great flue and stack described in the first paper[3] in order to prevent the escape of the arsenic. In accordance with an agreement entered into with the farmers, the smelter was shut down from July 1st to September 30th of this year, and when the plant was started on the latter date the smoke was supposed to no longer scatter poisonous substances over the valley, since it was passed through the flue intended for its purification. During the summer and autumn of this year there were very few cases of death among the animals of the valley and it was believed by the residents of the valley that there would be no more cases of sickness due to arsenic.

Two interesting exceptions were investigated in cases where the farmers thought that arsenical poisoning had occurred. A drayman in the city of Anaconda purchased a load of hay, supposed by him to have been grown during the year 1903. After feeding the hay to his horses for about a week one of them sickened and died, the most marked symptons before death being recurrent convulsions. A post-mortem examination showed the usual inflamed condition of the stomach, and the presence of a number of small ulcers, resembling those frequently observed in cases of arsenical poisoning. An analysis of the hay gave 0.0285 per cent. (285 parts per million) of arsenic trioxide. Various tissues of the animal were also analyzed and the liver found to contain 1.30 milligrams of arsenic trioxide to one hundred grams of tissue (13 parts per million). It seemed improbable that hay which contained so much arsenic could have been grown in the year when the smelter was closed for the three summer months, and upon investigation it was found that the hay had been grown about three miles north of the smelter during the preceding year.

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[1] THIS JOURNAL, preceding paper.

[2] Table 3; or Table I, preceding paper.

[3] THIS JOURNAL, 29, 971–3 (1907).

In October, a sheep owner who lived about twenty-eight miles from the smelter, and in a small valley somewhat protected from the smoke by an intervening range of hills, found that his grass was becoming exhausted. He rented a low field lying approximately fifteen miles northeast of the smelter, and drove his three thousand five hundred sheep from his home to this field, upon which there was a large amount of grass. After pasturing there for a week, a number of the sheep became sick, and the neighbors advised the owner to drive the flock to a feeding place farther from the smelter. On the way home five hundred sheep died, but during the next four weeks the mortality diminished. The total loss was six hundred and twenty-five animals. The case was investigated by the state veterinarian, Dr. M. E. Knowles, who decided that the sheep had died from acute arsenical poisoning. The four samples submitted by him for analysis gave the following results:

TABLE I.

Number.	Organ.	Parts As_2O_3 per million.
1	Stomach	3.1
2	Stomach	Trace
3	Stomach and liver	3.0
4	Stomach and liver	4.0

Claims were made that the sheep had died from poisoning caused by the alkali of the soil. A complete analysis of the soil, and a partial analysis of the stomachs of the sheep, showed that this was not true. It is a fact that the soil was high in the salts of the alkalis, containing 0.70 per cent. soda (Na_2O), 1.38 per cent. potash (K_2O), 0.40 per cent. sulphuric acid (SO_3), 0.00306 per cent. arsenic trioxide, 0.0118 per cent. copper, together with lead, a trace of antimony, etc.

A visit was made to the field to see if the cause of the death of the sheep could be determined. The grass was cropped very close to the ground, and over the lower part of the field there was a large amount of moss which had been greatly disturbed, presumably by the sheep during their feeding. On analysis it was found that the grass contained fifty-two, and the moss four hundred and five parts of arsenic trioxide in a million. It was therefore a reasonable assumption that the sheep had been poisoned at first by eating the grass, and in a greater degree by eating the moss at a time when the grass was nearly exhausted. It is probable that the sheep were very hungry when they first reached the field as they had lived for some time upon a meagre food supply.

There were no more complaints of serious damage from the farmers, so far as the effects of arsenic were concerned, until late in the autumn of 1904. It is true, that, while the effects of sulphur dioxide upon the plants had been moderated on the average, it had become more severe at many points some distance from the smelter. The charge began to be made by the farmers that the same was true of arsenic, and that symptons of arsenical poisoning had again manifested themselves in spite of the use of the big flue and stack. Chemical investigations were actively renewed in January, 1905, and have continued up to the present time. The results of the analyses of smoke and forage have been given in the previous papers of this series. A reference to these will show that enormous quantities of arsenic were thrown out by the high stack, and that large quantities were present on the vegetation.

Autopsies of a large number of animals were made, and many of the samples analyzed. Great care was taken with all of the analyses so that quantitative results of considerable accuracy might be obtained, and some of the precautions used will be described in a subsequent paper. The methods were first tested by analyses upon known amounts of arsenic. Various substances were used in the decomposition of the tissue, but the methods of Fresenius, von Babo, and Chittenden-Donaldson were adopted almost exclusively. All reagents were scrupulously purified from the most minute traces of arsenic, and were tested very frequently during the course of the analyses. All of the glassware, glass tubes, rubber tubes, porcelain-ware, etc., were tested to see if they would give traces of arsenic when used in the manner necessary for the tests. Berlin porcelain was used to the exclusion of glassware, except for the Marsh apparatus, which was made of Jena glass.

A modified Chittenden method which was much used in cases where little fat was present, consisted in putting 100 grams of the sample into a large casserole, and adding 100 cc. of nitric acid. The mixture was stirred frequently until it had become liquid, and was then heated on an asbestos board which rested on an electric stove. After heating for a half hour longer the solution was cooled, and thirty cubic centimeters of concentrated sulphuric acid added. The solution was heated until it began to turn brown, and then the steam of a dropping funnel was introduced through a hole in the watch glass cover, and nitric acid allowed to drop into the hot solution just rapidly enough to keep it from turning dark. After this addition has been kept up for some time, the solution could be evaporated (while adding nitric acid drop by drop) until the fumes of sulphuric acid appeared, without a blackening of the solution. A part of the sulphuric acid was then evaporated, nitric acid being occasionally added. The cooled solution was diluted and re-evaporated in order to remove oxides of nitrogen which might be present, and the cooled and diluted solution used for the determination of the arsenic by a modified Marsh method. The generator was kept active for six hours, stannous chloride being used to increase the activity of the zinc. It was found that this length of time was essential where weighable quantities of arsenic were determined. The best results were obtained by the use of a special fire-brick furnace with four very large burners. A second hard glass tube lying in a second furnace was connected with the first in order to test the completeness of the decomposition of the arsine, and arsenic was always found in this tube in cases where action in the generator became at all rapid.

The results of the analyses of a part of the animal samples are given in Table 2.

TABLE 2.—AMOUNTS OF ARSENIC IN THE TISSUES OF ANIMALS.

No. and organ.	Date.	Animal.	Distance.	Parts As_2O_3 per million.
	1902			
1 L	Sept.	Horse	3 NW	4.7
2 L	Sept.	Horse	2 SSE	1.1
3 L	Sept.	Horse	5 SE	2.8
4 L	Sept.	Horse	5 SE	0.8
5 L	Sept.	Cow	3 E	11.3
6 L	Sept.	Calf	3 S	6.2
7 L	Sept.	Calf	1.5 S	0.4
8 L	Sept.	Calf	1.5 S	0.3
9 L	Sept.	Steer	3 NE	8.6
	1903			
10 S	Oct.	Sheep	15 NNE	3.1
11 S	Oct.	Sheep	15 NNE	Trace
12 L & S	Oct.	Sheep	15 NNE	0.7
13 L & S	Oct.	Sheep	15 NNE	4.0
14 L	Oct.	Horse	1.5 NE	13.0
	1905			
15 L	Jan.	Filly	3 N	0.01
16 Lu	Jan.	Geld	5 E	7.1
17 S	Jan.	Geld	2 SW	0.01
18 L	Jan.	Cow	6 SE	3.3
19 L	Jan.	Geld	4.5 NNE	35.0
20 K	Jan.	Mare	14 NNE	13.3
[1]21 L	Jan.	Colt	2 S	2.6
22 L	Jan.	Cow	3 SW	1.6
[1]23 L	Jan.	Cow	3 SE	2.1
24 L	Jan.	Cow	5 NE	11.9
25 L	Jan.	Cow	5 NE	10.3
26 L	May	Steer	13 NNE	0.01
27 L	May	Cow	6 N	0.01
28 L	Nov.	Cow	13 NNE	10.00
29 L	July	Cow	2 S	7.4
[1]30 L	Jan.	Sheep	8 N	0.01

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[1] The shoulder of colt 21 was covered with a green fat which contained 288 parts of copper to the million. Sample 30 L contained 592 parts; and sample 23 L, 88 parts of copper to the million.

TABLE 2 (*Continued*).

No. and organ.	Date.	Animal.	Distance.	Parts As_2O_3 per million.
31 L	Jan.	Sheep	3 N	6.8
32 L	Jan.	Calf	2 S	1.5
33 L	Jan.	Calf	3 SW	6.5
34 L	Feb.	Calf	2 S	1.3
	1906			
35 L	Nov.	Geld	3 S	6.0
36 L	Oct.	Geld	4 N	3.4
37 L	Aug.	Mare	4.5 NE	4.4
38 L	Aug.	Geld	1.7 SSW	3.9
39 L	Aug.	Horse	5 NNE	16.1
40 L	Aug.	Horse	5 NNE	9.5
41 L	Jan.	Mare	5 NNE	1.3
42 L	Sept.	Geld	4.2 NNE	14.8
43 K	Jan.	Mare	15 N	2.1
44 L	Jan.	Mare	15 N	8.7
45 L	Jan.	Geld	10 NNE	7.6
46 L	Jan.	Geld	3 N	5.3
47 L	Feb.	Filly	4.5 NNE	3.1
48 L	Feb.	Filly	5 N	17.8
49 L	Feb.	Mare	4.5 NNE	8.7
50 Br	Feb.	Mare	4.5 NNE	4.5
51 H	June	Filly	4.2 NNE	460.0
52 L	Mar.	Horse	1.5 S	20.7
53 L	Aug.	Mare	12 NNE	4.99
54 B	Aug.	Mare	12 NNE	20.67
55 L	Sept.	Horse	4.5 NNE	Trace
56 L	Sept.	Mare	6.5 SE	52.5
57 L	Sept.	Geld	4.5 NNE	3.3
[1]58 K	Feb.	Colt	4.5 NNE	19.8
59 L	Feb.	Colt	10 NNE	Trace
60 L	Feb.	Colt	4.5 NNE	25.5
61 L	July	Colt	3 NNE	31.7
62 L	July	Colt	2 S	4.4
63 L	Nov.	Colt	9 NNE	2.6
64 L	Oct.	Colt	2 S	4.7
65 L	Aug.	Colt	8 NE	2.2
66 L	July	Colt	8 NNE	1.1
67 L	Feb.	Cow	10 N	11.8
68 L	Feb.	Cow	3 SSE	33.8
69 L	Nov.	Cow	13 NNE	10.0
70 L	July	Cow	3 N	14.2
71 K	July	Cow	3 N	6.2
72 L	July	Cow	3 N	63.12
73 L	Nov.	Cow	3 SSE	9.2
74 U	Nov.	Cow	3 SSE	16.0
75 L	Nov.	Cow	10 NNE	1.2
76 L	Nov.	Cow	4.2 NNE	10.4
77 L	Jan.	Steer	5 E	5.4
78 L	Oct	Calf	1.7 SW	16.2

TABLE 2 (*Continued*).

No. and organ.	Date.	Animal.	Distance.	Parts As_2O_3 per million.
79 L	Feb.	Calf	3 SSW	6.3
80 L	Jan.	Sheep	10 N	8.9
81 L	Aug.	Sheep	4.2 NNE	5.0
82 L	Sept.	Pig	1.7 SSW	Trace

L represents a sample of the liver; B, of the bone; Lu, of the lungs; U, of urine; H, of hair; K, of kidney; Br, of brain; S, of stomach. The animals represented by samples 1 to 42 were more emaciated on the average than those represented by samples 43 to 82.

The number of parts per million multiplied by seven-tenths gives the number of grains of arsenic trioxide to one hundred pounds of tissue. In this way a comparison may easily be made with the recommendation of the Royal Commission on Arsenical Poisoning:[1]

"In our view it would be entirely proper that penalties should be imposed under the sale of Food and Drugs Acts upon any vender of beer or any other liquid food or of any liquid entering into the composition of food, if that liquid is shown by an adequate test to contain 1/100 of a grain or more of arsenic in the gallon; and with regard to solid food—no matter whether it is habitually consumed in large or small quantities, or whether it is taken by itself (like golden syrup) or mixed with water or other substances (like chicory or 'carnos')—if the substance is shown by an adequate test to contain 1/100th grain of arsenic or more in the pound."

According to this recommendation a large number of the samples of liver given in Table 2 would be considered as deleterious when taken as food by human beings, and in one case a cow's liver contained forty-three times the maximum amount allowed in food by the commission. Flesh and also milk were found which exceeded the limit prescribed by the commission.

The livers of animals, according to Table 2, contained from a trace to 63.12 parts of arsenic trioxide to one million parts of tissue. The maximum number was obtained in a case of acute poisoning which occurred about three miles north of the smelter. This seems a strange case when it is considered that, although the grass of the ranch has usually contained a large amount of arsenic, at the time the cow died the percentage was relatively low, being between thirty and forty parts to the million.

An effort has been made to trace a relation between the quantity of arsenic ingested with the food, and that contained in the livers of the animals, but this has been impossible. It is true that the amounts of arsenic are larger on the average in cases where the animals were kept close to the smelter, but it is obvious that the condition of the animal is the more important factor in determining the amount of arsenic retained by the tissues.

[1] Final Report Royal Commission on Arsenical Poisoning, p. 50 (1903).

The amounts of arsenic present in the organs of the animals is in many cases small, yet no smaller than might reasonably be expected in chronic arsenical poisoning following the repeated and regular administration of moderate doses of arsenic. Before the time of this investigation, very little experimental work had been done on horses and cattle in which accurate analyses had been made of the organs following arsenical poisoning. In a case reported by the Russian Minister of the Interior, the liver of a cow which had been fed considerable amounts of arsenic for a period of six months, contained 0.13 part of arsenic per million. Spallanzani and Zappa[1] fed a cow from 0.4 to 0.5 gram (6 to 8 grains) of arsenic trioxide daily for 44 days and the following results in parts of arsenic per million were obtained from an analysis of the viscera:—stomach, 19; liver, 11; kidneys, 4.5; spleen, 7.6; lungs, 3; muscles, 3.8.

In order to see how the results of Table 2 would compare with those obtained from animals killed by arsenic, and also in order to secure data as to the poisonous dose, horses were fed upon arsenic in different forms. The doses given were large as the time for the experiments was very short. A horse was fed upon flue dust containing a total of 20.65 per cent. of arsenic calculated as trioxide, and 17.89 per cent. of soluble arsenic, also calculated as trioxide. Considering only the soluble arsenic, the horse was fed two grams of arsenic trioxide for eighteen days in addition to hay containing about 0.0030 per cent. In the liver was found 3.5 parts, and in the kidneys 18.0 parts per million, an amount for the liver which was less than the average of the values given in Table 2. A second horse was given 2.8 grams (0.1 oz.) of arsenic trioxide in two doses, on the first day mixed with bran, and on the second ingested as a drench. On the fourth day the animal died, and on analysis the liver was found to hold 8.7 parts per million. A third horse died on the third day after having been given two doses of 7.5 grams each, one on the first, and one on the second day. The liver contained 12.2 parts, while that of a sheep which had been fed arsenic for some weeks contained 11.9 parts to the million.

In taking samples during the first few years of the case, the more emaciated animals were usually selected, but beginning with January, 1906, a larger number of those that were fat and in a seemingly good condition were chosen. The result of this change of policy is shown in the table, where the average content of arsenic for 1906 is much higher than for previous years.

The elimination of arsenic probably begins very early and persists during the whole period of its absorption. In the human subject it often appears in the urine within five hours after ingestion, and may continue to be eliminated for thirty days after the last dose is taken. This is unusual, however, fifteen days usually sufficing to remove almost all of the arsenic from the human system. The difficulty in finding in the tissues any considerable amount of arsenic—an amount for example, sufficient to prove on the basis of a chemical analysis alone that death was due to arsenical poisoning, lies here. And where the case is one of chronic poisoning extending over a long period, and caused by a fairly constant amount of the poison being ingested daily, the isolation of an amount approximating a toxic dose is often impossible, simply because a really toxic dose was never taken at one time, and what was taken was partly excreted by the kidneys even before its absorption from the stomach and intestines was complete.

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[1] *Annal di Agricoltura*, 131, 25.

The proof of poisoning is complete, (1) "when the symptons known to be caused by the poison have been observed during life; (2) when the postmortem examination shows the presence of such lesions as it is capable of producing, and the absence of other causes of death; (3) when the toxic agent is demonstrated to be present in the cadaver or dejecta of the animal poisoned." It is not always possible to present evidence along all these lines, for it has often occurred, even with a poison so prompt in its action and of such certainty of detection as arsenic, that life may be prolonged for a sufficient length of time to permit the total elimination of the poison, and death results from its action by a continuation of the morbid processes which it established. Again one of the symptoms of chronic poisoning through arsenic is loss of appetite, so that often during the last few weeks or days of life, little or no food is taken. Then where the poison accompanies the food, and is proportionate to it in amount as in the cases at issue in this investigation, failure to take any considerable amount of food during the last few weeks of life, stops the ingestion of the poison and allows the system to expel all or nearly all the substance before death ensues. In certain of the cases given in Table 2, animals apparently in a diseased condition were slaughtered. This was true of cow 31, whose liver showed 6.8 parts of arsenic trioxide to the million, or a total of 0.5 grain for the entire organ. It also carried 1.5 grains of copper. Though considerably emaciated, the large quantity of food in the stomach showed that the animal had not lost its appetite, and this was substantiated by the statement of the owner. A sheep from ten miles north of the smelter, on the other hand, though slaughtered, was virtually in a dying condition, and had evidently partaken of but very little food for some time. Only a slight trace of arsenic could be detected in the liver, but a surprisingly large amount of copper was present. Still the animal was undoubtedly suffering from arsenical poisoning, and the reason so little arsenic and so much copper were found is that arsenic is rapidly eliminated while copper is very slowly excreted, being retained mainly by the liver. In some of the cases very large amounts of copper were found in the fat, a part of which had a greenish tinge.

Moderate amounts of arsenic continuously administered, cause an increase in body weight and much increased storage of fat between the muscles as well as around the kidneys. While this is true in general of all animals it is notably true of herbivorous animals. In minute doses arsenic improves the appetite and increases both the motions and secretions of the stomach and duodenum; and since there is no considerable accumulation of arsenic, due to its rapid elimination through the excretory channels, medicinal or smaller doses may be administered daily over a prolonged period without showing harmful effects.

Reliable data on the subject of the arsenical poisoning of live stock are very meagre, and most of the statements found in the usual text books are so conflicting that a definite conclusion as to what may be considered a fatal dose of arsenic for a horse, cow, or sheep, cannot be reached through them alone. Much of the most reliable work has appeared in the chemical journals.

Spallanzani and Zappa[1] fed moderate amounts of arsenic continuously to a "Durham" cow for 46 days, when death resulted. From 0.5 to 3.0 grams (7.7 to 46.3 grains) of arsenious oxide were administered daily, the dose being gradually increased to the maximum of 3 grams, when the animal died. Spallanzani concludes from this and other experiments that cattle will take without injury, over indefinite periods, doses of 0.5 to 0.7 gram (7.7 to 10.8 grains) of arsenic trioxide per day, and may indeed increase in weight under it. They first show toxic symptoms with doses of 1 gram (15.4 grains) per day. The maximum non-toxic dose for cattle is given as about 0.00015 part of arsenious oxide per day for 100 parts body weight, or 10.5 grains per day for an animal weighing 1,000 pounds.

The results cited in the last paragraph are well in accord with the results of the investigations of the writers as made on the animals of smelter districts. A review of the literature of the subject reveals such great discrepancies in regard to the fatal dose that it is almost impossible to believe all of the results cited. On the one hand, we have the work of Cameron[2] which shows that ten cows were killed by one dose for each cow, of 8.4 grains of arsenic trioxide in the form of sodium arsenite. In contrast with this case, which seems to be authentic, we have the statement attributed to Hertwig[3] that he gave arsenic to eight different horses in doses beginning with twenty grains but increasing to a dram, and continued these doses for from 30 to 49 days with no bad effects, in fact, "the condition was improved."

On account of the unsatisfactory state of the literature of this subject, it was decided to inaugurate further experiments to test the effects of different doses upon cows and horses. However, at this time it was not found possible to meet the expense of such an undertaking, so the work was done upon sheep.

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[1] *Annal di Agricoltura*, 131, 25.

[2] *Analyst*, 1888.

[3] *Veterinarian*, 1843, p. 345.

Results of Work on Sheep.—Four of the healthiest sheep were chosen from a flock of several hundred. They were fed upon local arsenic-free hay at Palo Alto, California, and the doses given in starch capsules as follows:

TABLE 3.

	Dose. Arsenic trioxide.	Weight at beginning.	Form of arsenic.
1..........	0.181 gram twice a day	95 lbs.	Arsenic trioxide
2..........	0.123 gram once a day	87.5 lbs.	Sodium arsenite
3..........	0.055 gram once a day	115 lbs.	Sodium arsenite
4..........	0.021 or 0.090 gram once a day	90.5 lbs.	Sodium arsenite

The results of this experiment are given graphically in Fig. 1. Sheep No. 4 was given daily doses of 0.021 gram for 35 days, when an increase to 0.090 gram was made, because it was believed that upon the smaller dose the sheep would not die before the conclusion of the experiment at the end of ninety days. This was the only sheep that did not die, but that

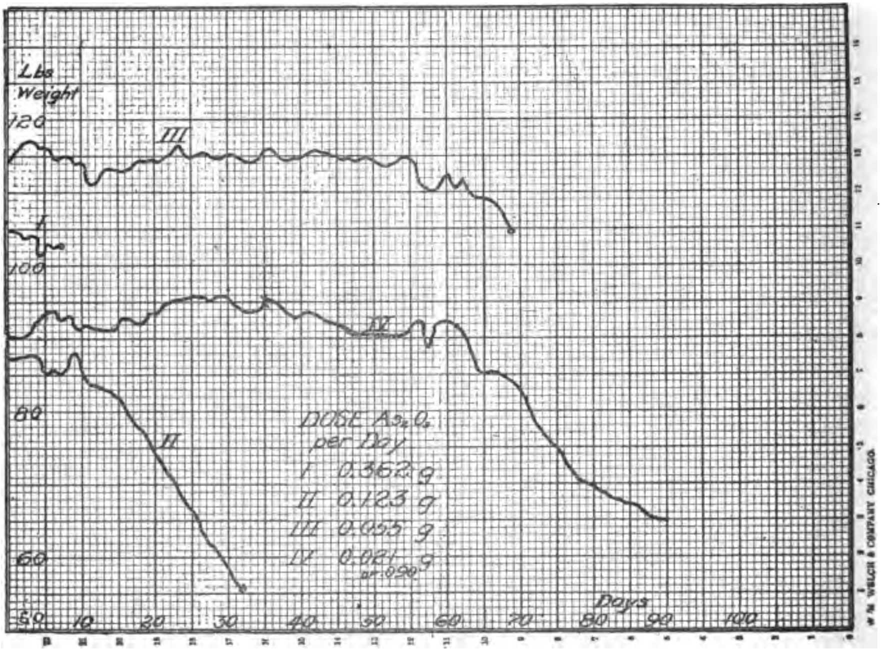

Fig. 1.—Effect of arsenic trioxide on the weight of sheep.

NOTE.—Curve I is raised ten units of weight in order not to interfere with Curve IV.

death would have resulted soon after the expiration of the time set for the close of the experiment is evident from the curve (*IV*) which shows a rapid decrease in weight toward the end of the period.

The experiment shows that 46 milligrams (0.7 grain) of arsenic trioxide per day, administered in the form of arsenite of sodium, to 100 pounds of body weight, is sufficient to cause the death of a sheep. The perfectly regular way in which the arsenic reacted upon the sheep as expressed in the curves of the body weight, at least suggests strongly that the result was not due to individual susceptibility.

The case of sheep No. 2 was an instructive one. It was given a dose of 0.123 gram per day for twenty-five days, and lived eight days longer before death ensued. No food was taken during the last thirteen days, and practically none for eighteen days, though fresh food was offered three times each day. During the eighteen days the animal was practically in a comatose condition, suffering no pain, and reclining upon its side most of the time. On dissection the intestines were found absolutely empty, since an attack of diarrhea had lasted for eight days, while the stomach was greatly distended and packed with solid food. Digestion had been absolutely suspended for a long time, and decomposition of the stomach lining had already begun. At the beginning of the feeding the animal weighed 87.5 pounds, and at the end 56 pounds, of which eight pounds was undigested food packed in the stomach. A number of the doses of arsenic were found undigested in this organ. To each million parts the liver contained a trace, the tissue of the stomach 3.0 parts, and the brain 4.2 parts, certainly a peculiar distribution of the poison. Evidently little arsenic had gone into the circulation from the stomach for a considerable period, so the liver had been able to eliminate most of the arsenic. The post-mortem appearance of the organs of the sheep, taken as a whole, was that of acute rather than long standing chronic arsenical poisoning.

The question of the amount of arsenic which will kill a farm animal, if fed daily, is a very important one to the chemist who undertakes to investigate the conditions existing in smelter regions. The effects depend so greatly upon the conditions that even after such an extensive investigation as that carried out by the veterinarians, pathologists, bacteriologists and chemists, upon the present case, no very definite statements can be made in regard to this point. A study of Table 1 of the second paper of this series will give some idea of the poisonous dose, for on almost all of the ranches listed, animals have been supposed to die from arsenical poisoning. On the other hand, there is almost no place in the farming district where some of the animals will not survive. As has already been indicated, there is comparatively little sickness during the late spring and summer, but by November a large number of animals are affected, if they are allowed to run upon the pastures.

The following table gives the average amounts of arsenic trioxide in the grasses analyzed during the last three years:

TABLE 4.—AVERAGE AMOUNTS OF ARSENIC TRIOXIDE IN GRASS AND HAY.

	As_2O_3 in parts per million.		Grains to 25 pounds food.	
Year.	Grass.	Hay.	Grass.	Hay.
1905	106	45	18.6	7.9
1906	155	42	21.7	7.4
1907	100	..	17.5	...

The column "Grains to 25 pounds food" is supposed to represent the amount of arsenic taken in a day's feeding, since this is the amount of dry matter in the daily ration for this region. On the average, then, the daily ingestion of arsenic is about 20 grains for grass, and 7.5 grains for hay. The amount varies from a minimum of 1.75 grains for young meadow grass taken two miles south of the smelter, to 271.4 grains for a sample taken in the smelter field one fourth mile from the old low stacks. The average for the grass is interesting in comparison with the statement of Spallanzani and Zappa, that one gram (15.4 grains) per day is the minimum amount which can give rise to the toxic symptoms in cattle.

The farmers claim that animals which are shipped into the valley succumb more quickly than those that have lived for some time in the district, and this is undoubtedly true. It might be assumed that this means the animals able to survive are those of great individual resistance and tolerance with respect to arsenic, an assumption which is true in part; but, in addition to this, there is little doubt that tolerance is gradually established to a certain extent by the use of the poison, as is the case with human beings.

In order to see what proportion of the arsenic in the plants would be soluble in the digestive juices of the animals, and thus act as a poison, two digestion experiments were made. A sample of hay or grass, 300 grams, was digested at 38° C. for two days with a glycerol extract of the mucus lining of the abomasum, the mixture being made acid with hydrochloric acid. Then the liquid was made slightly alkaline with sodium carbonate, digested five days with the glycerol extract of two pancreas glands, and toward the end of the time putrefactive bacteria were added. The results were as follows:

	Grass. 5 mi. N.	Hay. 4 mi. N.
Percentage of soluble As_2O_3	0.0242	0.0058
Percentage of insoluble As_2O_3	0.0019	0.00114
Total per cent. As_2O_3	0.0261	0.0069
Percentage of total arsenic which is soluble	92.6	83.6

The greater amount of arsenic is undoubtedly in a poisonous form.

The Distribution of Arsenic in the Organism.—Several animals were sampled in such a way that portions of nearly every organ were taken, but only one set of data will be presented—for a case in which the distribution seemed normal in comparison with our other results, although the amount of arsenic is lower than the average. On November 4, 1906, a horse was killed and sampled. In general condition, the animal was unthrifty, and its coat was very rough. The clinical symptoms were redness in the stomach and intestines, congestion of the lungs and pleura, congestion of the brain and bladder, slight congestion of the kidneys, catarrh of the intestines and an enlarged spleen. The results of the analyses of the organs are presented in Table 5.

TABLE 5.—THE DISTRIBUTION OF ARSENIC IN THE TISSUES OF A HORSE IN A CASE OF CHRONIC POISONING.

No.	Food or organ.	As_2O_3 in parts per million.
1	Grass No. 1	45.00
2	Grass No. 2	107.00
3	Dust from hay	9190.00
4	Ulcer in nose	658.00
5	Contents stomach wet	25.00
6	Contents stomach dried	398.00
7	Urine	59.00
8	Hair of tail	58.00
9	Liver	6.00
10	Thyroid gland	6.00
11	Stomach	4.70
12	Spleen	4.60
13	Pancreas	4.40
14	Small intestines	4.00
15	Brain	3.30
16	Spinal cord	2.60
17	Muscles	2.50
18	Lungs	2.20
19	Bones	2.20
20	Heart	2.10
21	Bladder	1.40
22	Kidney	1.40
23	Right parotid	0.80
24	Fat	0.70
25	Suprarenal	0.06
26	Fluid around heart	0.05
27	Blood	0.03

The horse had fed upon grass and hay containing from twenty to forty-five parts of arsenic trioxide to the million for a period of some months, and for three days had been eating grass containing 107 parts. For several years it had been fed upon grass and hay containing arsenic in varying amounts. Dust shaken from the hay stack in the field where the horses were pastured for three days, contained 9190 parts of arsenic trioxide.

Arsenic in Milk.—Ten samples of milk, most of them mixtures from several cows, were obtained by milking directly into bottles provided with glass stoppers. The analyses gave:

Table 6.—Arsenic in Milk.

No.	Date, 1906.	Distance from smelter.	No. of cows.	Parts As_2O_3 per million.	Grains to 100 gallons.
1	Sept. 21	4.5 NNE	5	2.94	17.7
2	Nov. 3	3 E	1	0.47	2.83
3	Nov. 3	6 NNE	1	0.70	4.00
4	Nov. 3	4.5 NNE	2	0.18	1.08
5	June 28	4.5 NNE	1	1.40	8.42
6	June 27	5 E	1	1.00	6.02
7	July 2	3 SE	1	4.20	25.28
8	June 28	3 N	5	3.40	20.47
9	June 23	3 W	1	5.70	34.30

The Arsenic Content of Ulcers of the Nose.—A complaint among the horses of smelter regions called the "sore nose" has been observed by the writers in the Anaconda and Salt Lake regions. It is also reported that the same disorder is found in Great Falls, and among the horses of the smelting region in Cornwall. Of the persons who worked on the smelter stacks in determining the arsenic content of the smoke, two became affected with an arsenical rash upon the face, while the nostrils of the third were almost closed by a swelling caused by the irritant action of the flue dust. In the case of horses, one nostril may become closed almost absolutely on account of an ulcer which forms on the lower portion of the nasal partition. Several of these ulcers were taken from the nostrils of different horses and analyzed with the following results:

No.	Distance.	Parts As_2O_3.	No.	Distance.	Parts As_2O_3.
1	2 miles S	254	4	2 miles S	902
2	4.5 miles NNE	587	5	3 miles SW	545
3	3 miles SE	1015			

Undoubtedly the highly arsenical dust from the hay and grass lodges in a fold of the nostril and irritates the mucous membrane until the nose scab is formed. The dust from the hay of the ranch where samples 3 and 5 were obtained, contained 9190 parts of arsenious oxide per million.

In order to see if the cases observed in Salt Lake could be due to this cause, samples were taken in different parts of the district. These samples, taken September 3, 1905, contained from ten to sixty parts of arsenic trioxide to the million, results which would indicate that sufficient arsenic is present to cause the observed effects.[1]

Arsenic in the Hair.—According to the evidence of Mann[2] arsenic is localized in and eliminated by the hair. Large amounts of arsenic were found in the hair of animals of the Anaconda region. The hair of the tail of one horse contained fifty-eight parts of arsenic trioxide to the million, an amount ten times as great as that found in the liver. The hair of a colt contained 605 parts, the liver 4.4 parts, and the bone 13.2 parts, while the grass in the field where the colt was feeding contained only ten parts per million. The hair of a filly pastured five miles north of the smelter gave 460 parts of arsenic. The case is more complicated than those investigated in England, since an unknown fraction of the arsenic in the hair was undoubtedly deposited from the atmosphere. Nevertheless, the results are striking and important.

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[1] For other results from this district see preceding paper, Table VII.

[2] Report of the Royal Commission, p. 13; and Minutes of Evidence, Vol. 1, p. 139.

Normal Arsenic.—Attempts have been made to show that the amounts of arsenic present in the tissues of the animals of smelter regions represent what may be called normal arsenic. This is certainly a perversion of the conclusions of Gautier and Bertrand, for the results obtained by them were of a totally different order of magnitude from those obtained in forensic cases; and they found arsenic only in the thyroid, thymus, brain and skin. Even these results have been criticized by Kunkel,[1] Hödlmoser,[2] Cerny,[3] Stevenson and Mann.[4] The latter writers claim that the arsenic present is wholly adventitious.

No attempt was made by the writers to test Gautier's conclusions, but about forty-five livers from Palo Alto, California, New York City, and Missoula, Montana, were analyzed, using samples of from one hundred to eight hundred grams. Using tests which would detect the presence of 1/1000 mg. of metallic arsenic, in no case was arsenic found. This is sufficient proof that the question of normal arsenic need not come into smelter smoke investigations.

Symptoms.—The following three examples may be taken as typical cases which together exhibit the range of important symptoms which have appeared in connection with arsenical poisoning in the Deer Lodge Valley.

Case (*a*).—The first example is that of a roan mare owned by a farmer living about eight miles north of the smelter. She was eight years old, weighed thirteen hundred pounds, was sleek and fat, and so far as outward appearances went, perfectly sound. The owner stated in answer to questions, that the animal had fed rarely on pasture but almost entirely on hay, of which she ate much more than the average ration. For nearly a year, however, she had been failing in strength, and was no longer able to do an ordinary day's work, profuse perspiration and total exhaustion following any unusual exertion. An examination showed a "sore nose" scar in one nostril.

The animal was shot and the autopsy made immediately thereafter. The urine was white in color and heavily sedimented; the heart "flabby" and larger than normal; the lungs were covered with a mattery adherent exudate and were "flabby," due to the blocking of the bronchii with a yellow caseous substance, and the escape of air into the tissues; the liver weighed 17 pounds, 7 pounds above normal; the mucous membrane of the stomach was reddened over certain areas in the fundus; the small intestines showed a great many extensive diffuse red patches; the large intestines were generally badly reddened, and here and there distinctly eroded. An unmistakable odor of garlic was observed when the intestines were opened. The mucous membrane of the uterus and bladder was notably reddened, and the right ovary was gorged with a deep red gelatinous substance. The bone marrow was of a deep yellow color, due to a quantity of yellow oil which filled the interstices and retained its liquid character at ordinary temperatures.

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[1] *Z. physiol. Chem.*, 44, 511–529 (1905).

[2] *Ibid.*, 33, 329-344 (1901).

[3] *Ibid.*, 34, 408 (1901).

[4] Minutes of Evidence, Royal Commission on Arsenical Poisoning.

Case (*b*).—The second is a colt, one year old, which was posted two miles south of the smelter on July 3, 1906. It began to appear unthrifty during the fall of the preceding year while on the hill pastures, and at no time thereafter did it show a normal growth. The autopsy showed that this was a case of remote chronic rather than of acute poisoning. The secreting mucous membranes throughout the body were reddened in patches, but only slightly. The hair was shaggy and lusterless, and the whole organism weakened and emaciated.

Case (*c*).—The last case is that of a colt, eleven months old, which had developed normally during the sucking period of six months, when it was weaned and removed to an adjoining pasture early in the month of March. From that time until July 1st it subsisted on hay from a stack in the field. On the date mentioned, following an effort to rope it, the colt had a "fit" and died in convulsions. The stomach showed three distinct, crater-like ulcerations and extensively irritated areas, especially in the folds. The lungs were badly discolored as in necrosis or fatty degeneration. The organ was certainly badly affected, and as soft as a partially decomposed organ. The intestines were highly inflamed, often for five to eight inches in one place, and the whole of the small intestine was covered with inflamed patches.

The first of the cases cited is apparently one in which the arsenic showed its usual stimulating action, strengthening the appetite, promoting the digestion, causing the deposition of much intestinal fat and giving a sleek appearance to the subject. The action was proceeding beyond this stage however, and a breaking down of many of the organs was in evidence. This was a case of progressive chronic poisoning, shown further by the large amounts of arsenic in the bone (20.67 parts per million).

The second case seems to be one of true chronic poisoning which evidently took another course, the stimulating effect being constantly overshadowed by the more destructive action of too large doses. The organism was too weak to recover, even after loss of appetite reduced the ingestion of the toxic agent to a minimum. The stomach was nearly empty, and the liver carried only very small amounts of arsenic, while the storehouses for arsenic in the organism, the bone and hair, showed excessive amounts. The analytical results were: hair, 605 parts; bone, 13.2 parts; liver, 3.3 parts; and heart, 1.7 parts of arsenic trioxide per million.

The third case is one of recent chronic poisoning, leading rapidly to a culmination in a way truly characteristic of the substance. The liver of this colt contained 31.7 parts, and the kidneys, 2.4 parts of arsenic trioxide per million.

During a considerable time the writers were associated in this work with Dr. D. E. Salmon, of the Bureau of Animal Industry, who very kindly prepared an outline of the more prominent symptoms of the animals as they appeared to him, for use in this publication. These are given as follows:

Symptoms of the Chronic Arsenical Poisoning caused by the Vegetation of Smelter Regions.

Horses.—1, Raised red line at the base of incisor teeth; 2, breath of a garlic odor; 3, loss of spirit, vigor, and endurance; 4, falling of hair; 5, retention of old hair; 6, ulcers of the nose; 7, weakness and imperceptibility of pulse; 8, erosions on the outer side of gums; 9, puffiness above the eye; 10, rough lusterless hair; 11, partial paralysis of hind limbs; 12, with more acute form: (*a*) Difficult breathing, (*b*) labored action of heart, (*c*) dilation of pupils of the eyes, (*d*) partial paralysis of the diaphragm and costal breathing.

Cattle.—1, Shrinkage of milk within a day or two after smoke has been over pastures; 2, salivation and drooling; 3, constipation; 4, rough scurfy coat; 5, eyes red, inflamed, and weeping; 6, loss of appetite; 7, diarrhea when disease becomes more pronounced; 8, tucked up abdomen; 9, loss of flesh; 10, weakness, loss of vigor; 11, cough; 12, breath of garlic odor; 13, droppings covered with mucus; 14, abortion and failure to breed.[1]

In an examination of the animals of a smelter district the chemist may be greatly aided by a careful post-mortem examination, and by the histological study of small specimens taken for this purpose. The most important features to be seen in the sections taken for microscopical investigation are: proliferation of the connective tissue cells, degeneration and desquamation of the tubules in the kidneys, congestion or diapedesis, the occurrence of hemorrhagic areas, and occasionally a total disintegration of the cells. In some cases there is very marked fatty degeneration. The kidneys show these symptoms more prominently than the other organs.

The Anaconda case is of interest not only to the toxicologist, but also to the industrial chemist and the metallurgist, since arsenic in a great number of cases is a constituent of the metallic sulphides, especially those of copper. Large amounts of arsenic are given off by the smelters of Salt Lake, Utah; Everett, Washington; Great Falls, and Butte, Montana; and from many of the smelters of Germany, England, and other countries. In 1854 and 1875, Haubner investigated the smelter smoke disease in the Freiburg district, and various other cases have been studied to a slight extent.

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[1] The diminution in the human birth-rate was noticed during the Manchester epidemic, and the results tabulated by J. Niven. See Royal Commission on Arsenical Poisoning, Minutes of Evidence, Vol. II, Appendix 17, p. 196.

In the decision of Judge Marshall of the Circuit Court of the United States as made November 5, 1906, the conditions existing in the Salt Lake smelter district are described in such a way as to make an interesting comparison with the results of this series of papers. In speaking of the sulphur dioxide he says: "This gas is heavier than air, and when cooled, falls to the ground at a distance from the smelters dependent upon the air currents. When it is brought in contact with moisture, either in the form of rain, freshly irrigated ground, or the moisture present in growing plants and the foliage of trees, sulphurous or sulphuric acid is formed, which is destructive to vegetation. Besides the emission of gas, some flue dust is emitted from the smelters which contains perceptible quantities of arsenic resulting in the death of horses and cows."

In conclusion, the writers wish to thank Dr. John Maxson Stillman for the many suggestions which have been helpful in this work.

THE UNIVERSITY OF MONTANA AND STANFORD UNIVERSITY,
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THE MARSH TEST AND EXCESS POTENTIAL.

(FIRST PAPER.[1])

THE QUANTITATIVE DETERMINATION OF ARSENIC.

BY W. D. HARKINS.

Received May 14, 1909.

Introductory.

The most widely used method for the determination of small quantities of arsenic is the separation as arsine suggested by Marsh,[2] together with the decomposition of this gas in a heated glass tube as recommended by Liebig.[3] An excellent review of the history of the development of this method has been given by Lockemann.[4]

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[1] Presented at the New York meeting of the American Chemical Society, December 28, 1906, and in part at the December, 1905, meeting of the Stanford Chemical Society.

[2] *Ann.*, 23, 207 (1837).

[3] *Ibid.*, p. 217.

[4] *Z. angew. Chem.*, 18, 416 (1905).

In the year 1902 the writer attempted to utilize the Marsh method for the direct determination of the arsenic contained in the acid extracts from soils, but found that the amounts of arsenic recovered were entirely too small. This was explained by the work of Parsons and Stewart[1] and other investigators[2] as due to the retentive effect of the iron present in the solution. According to Headden and Sadler[3] a successful determination by this method can be made only in the absence of iron, copper, platinum and their salts.

In spite of the exidence cited above, and that of other observers,[4] A. H. Allen[5] recommends that zinc should always contain a certain amount of iron to insure a regular evolution of hydrogen, and Gautier[6] advises that platinic chloride be added in order to make the zinc active. Even in what he claims to be his most delicate method,[7] he precipitates the arsenic together with ferric hydroxide and adds the solution of this precipitate, containing about 0.1 gram of iron, directly to the Marsh generator.

Retention of Arsenic by Iron and Other Metals.

In view of these facts it was thought advisable to repeat a portion of the work of Parsons and Stewart. The experiments confirmed their work in every respect, showing that approximately the same percentages of arsenic were held back by the iron as those given in their paper. The results obtained, together with a few of the data given by Parsons and Stewart, are appended in Table I:

TABLE I.—RETENTION OF ARSENIC BY IRON.

Wt. Zn.	Reagent.	Wt. Iron.	Arsenic.		Per cent. Found.	Time. Hrs.
			Taken.	Found.		
35 g.	H_2SO_4	0.160 g.	1.88	1.00	53	6
35	HCl	0.400	1.88	0.72	38	5
35	H_2SO_4	7.000	1.88	0.30	16	6
35	HCl	7.$FeCl_3$	1.88	0.25	13	6
35	H_2SO_4	0.150	0.80	0.52	65	6
35	H_2SO_4	0.150	0.93	0.55	59	4
		Parsons and Stewart.				
30		0.060	5.00	3.45	69	
30		0.300	5.00	2.70	54	
30		1.500	5.00	2.95	59	
30		6.000	5.00	1.60	32	

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[1] THIS JOURNAL, 24, 1005 (1902).

[2] Wöhler, *Ann.*, 23, 217 and 223 (1837). Santermeister, *Chem.-Ztg.*, 15, 1021. J. Thiele, *Chem. News*, 67, 125 (1893).

[3] *Am. Chem. J.*, 7, 341.

[4] O. Hehner, *J. Chem. Soc. Ind.*, 20, 194 and 200. Chapman, "Reports of the Royal Commission on Arsenical Poisoning," Vol. II, page 84.

[5] *J. Soc. Chem. Ind.*, 21, 94 (1902).

[6] *Bull. soc. chim.*, 27, 20–21, 1030–34 (1902). *Ann. chim. phys.* (5), 8, 384 (1876).

[7] *Compt. rend.*, 137, 158–63. *Bull. soc. chim.* (3), 29, 859–863.

cc. of concentrated sulphuric acid mixed with 25 cc. of water were added to the generator. At once, when all the zinc was dissolved, the burners of the fire-brick furnaces were extinguished, the tile lifted from the furnaces, and the tubes cooled as quickly as possible. If this is not done, air will draw back into the apparatus and water vapor be formed and condensed, thus spoiling the determination. In cases where time is an object, the generator should be heated from the beginning.

After a series of preliminary experiments the results given in Table III were obtained:

Table III.—Effect of Heat upon the Retention of Arsenic by Iron.

Wt. zinc. Grams.	Time cold. Hours.	Iron added. Gram.	Time 100°. Hours.	Arsenic found. Milligrams.	Arsenic taken. Milligrams.
35	8	0.0	0.0	1.87	1.88
30	5	0.0	0.0	1.84	1.88
30	5	0.075	1.5	1.85	1.88
50	1	0.400	6.5	1.82	1.88
30	3.5	0.300	4.5	1.87	1.88
35	4.0	0.160	2.5	1.87	1.88
40	1.0	0.160	3.0	1.86	1.88
40	0.5	0.400	2.5	1.86	1.88
40	0.5	0.400	4.0	1.89	1.88
40	0.5	0.400	4.0	1.90	1.88
40		0.400	2.0	1.80	1.88
40		0.400	2.0	3.76	3.76
40		1.000	2.0	3.70	3.76

A comparison of these results with those given in Table I shows that heating the generator practically doubles the amount of arsenic reduced. It is evident that the directions which usually accompany the description of the Marsh test, namely that the generator be kept cold, are certainly erroneous and just the opposite of the best procedure. The directions should say that the concentration of the sulphuric acid present should be kept small near the beginning of the determination. For this reason hydrochloric acid is the better acid to use at first. The addition of moderately concentrated (1 : 1) sulphuric acid toward the end of the test improves the results, and the acid does not prove injurious by a resulting reduction.

In several cases, where the arsenic was deposited with extreme rapidity, a part of the mirror was a dark brick-red. This was not due to selenium, since the latter metal was not present. It is possible that this red substance was an allotropic modification of arsenic. In these experiments a white crystalline deposit was often obtained between the gas flame and the arsenic mirror. It is much less volatile than the arsenic, and can easily be separated from the latter by cutting the tube at the proper point. In appearance it is somewhat similar to that obtained when aluminium is used in the place of zinc in the generating flask. These deposits will be collected until a sufficient amount is obtained for the determination of the composition of the crystals.

The Separation of Arsenic by the Addition of Salts to the Generator.

The purest zinc which can be purchased dissolves in pure sulphuric acid with extreme slowness. If the salt of a metal which lies lower in the electromotive series is added to the acid it is found that in almost all cases the metal precipitates upon the zinc, but in such a way as to leave a part of the zinc surface in contact with the solution. If the metal thus precipitated has a lower excess potential than the zinc, which is the case with all of the metals considered in this paper with the exception of mercury, it would be expected that hydrogen would be liberated more easily from the surface of the second metal. In such cases we find that the zinc dissolves more rapidly than before, except that when salts of iron are added without vigorous stirring a considerable time often elapses before its effect is perceptible.

We may assume that the mechanism of solution of the zinc is now as follows: positively charged zinc ions pass from the surface of the zinc into the solution, and positive hydrogen ions are deposited upon the surface of the other metal, which for convenience we may consider as platinum. Gaseous hydrogen soon escapes from the surface of the platinum, and the mechanism of the reaction is the same as though the zinc and the platinum were connected by a wire, lying outside the solution. The system is a galvanic cell in which the zinc is the negative pole. So far as the platinum is concerned, however, the conditions are practically the same as if it were the cathode in an electrolytic cell containing sulphuric acid as an electrolyte. With such a system the reduction may take place either at the surface of the zinc or of the platinum electrode. If at the latter surface only, we have a case of cathodic reduction similar to that described by Tafel[1] or by Haber,[2] except that the depolarizer is itself a weak electrolyte in the case under investigation.[3] If we assume that the reduction takes place upon the surface of the cathodic metal, the reducing power should be related in some way to the value of the cathode potential. This potential depends upon the current density, the concentration of the oxide of arsenic, and the value of the excess potential for the particular metal. The value of the cathode potential (E) is given by the equation of Haber[4] for the case where no free hydrogen is liberated,

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[1] *Z. physik. Chem.*, 34, 197 (1900).

[2] *Ibid.*, 32, 193 and 271 (1901); 47, 257 (1904).

[3] Luther and Schilow, *Z. physik. Chem.*, 46, 777 (1900). This, of course, makes *possible* the direct electrolytic separation of arsenic, provided that the conditions are favorable. That arsenic is precipitated as a metal when the reducing action in the generator is small is well known (Parsons and Stewart, *loc. cit.*).

[4] *Z. physik. Chem.*, 47, 259 (1904).

$$E = x(\mathrm{RT}/n \ln I/C_{\mathrm{M}}C_{\mathrm{H}^{\cdot}} - \text{const.}),$$

where I is the current density; C_{M}, the concentration of the substance to be reduced; $C_{\mathrm{H}^{\cdot}}$, the concentration of the hydrogen ion; x is a number greater than one, whose value depends upon the value of the excess potential for the metal, and the subtractive constant represents the catalytic influence of the cathode metal upon the reduction in question.

From a theoretical standpoint, the simplest case for investigation would have been the reduction of the oxide of arsenic in an electrolytic cell,[1] with a high concentration of arsenic, vigorous stirring, and a relatively low current density. However, since the work was undertaken at the beginning in order to increase the accuracy of the quantitative determination of small (but still weighable) amounts of arsenic by the ordinary Marsh method, the most favorable conditions for the proof of the theory were not chosen, but instead a much more complicated system was used in which the concentration of the oxide of arsenic was low, and the current density large. Of the factors in the determination of the potential at which the hydrogen is liberated, the excess potential, the current density, and the catalytic action of the metal may be varied; but since nothing is known in regard to catalyzers for this reaction it was decided to work by choosing the first two factors properly and neglecting the last.

That arsenious oxide could be more readily reduced to arsine in the Marsh generator if the salt of a metal other than zinc was added, was suggested in 1893 by Thiele.[2] In trying to determine large amounts of arsenic he found that he could not get a complete reduction of the arsenic unless stannous chloride was added toward the close. Preliminary experiments made upon the basis of these suggestions showed that arsenic can be quantitatively separated from iron or *other injurious metals* by the addition to the solution of salts of bismuth, tin, lead, and cadmium.[3]

In these experiments dilute sulphuric acid was used, of the concentrations advised by Chittenden and Donaldson, though in some instances hydrochloric acid was added to hasten the solution of the zinc. When salts of lead were added to the generator, hydrochloric acid was always used, since in this case sulphuric acid acts slowly upon the zinc. Forty grams of zinc were used for each determination, and enough of the stannous chloride or other salt added to make the zinc active. The arsenical solution, together with the iron and more of the stannous chloride, was then added drop by drop. By the continuous addition of more acid and stannous chloride the action was kept as rapid as was possible without the loss of arsenic from the heated glass tube, until the zinc was almost

[1] Thus eliminating any possible reduction by the zinc.

[2] *Chem. News*, 67, 125 (1893).

[3] Chapman and Low, *Analyst*, Jan., 1906.

all dissolved. In this way it was found that weighable quantities of arsenic could be separated quantitatively from as much as 0.300 gram of iron. It is probable that the separation can be made also from a larger amount, but this was not investigated. It should be remembered that, according to the work of Parsons and Stewart, as little as 0.060 gram of iron is sufficient to prevent the reduction of thirty-one per cent. of the arsenic present.

TABLE IV.—EFFECT OF STANNOUS CHLORIDE AND OTHER SALTS UPON THE RETENTION OF ARSENIC.

No. of exp.	Weight of iron or other element.	Weight of $SnCl_2$ or other salt.	Arsenic taken. Milligrams.	Arsenic found. Milligrams.
1	0.3126 g. Fe	2.0 g. $SnCl_2$	0.75	0.75
2	0.3126	2.0	0.75	0.74
3	0.3126	1.5	0.75	0.75
4	0.3126	1.5	0.75	0.73
5	0.1160	2.0	0.75	0.74
6	0.0600	2.0	0.75	0.73
7	0.3200	4.0	1.86	1.81
8	0.2250	2.0	1.86	1.85
9	0.1550	2.0	1.86	1.84
10	0.1550	2.5	0.93	0.93
11	0.1550	2.5	4.65	4.58
12	0.1550	3.0	0.93	0.91
13	0.1550	2.0	0.93	0.90
14	0.155	4.0	4.65	4.70
15	0.155	No salt	4.65	(3.38)
16	0.155	No salt	93.60	(72.40)
17	0.155	5.0 g. $SnCl_2$	93.60	91.40
18[1]	0.170	5.0	112.40	113.50
19[1]	0.170	5.00	112.40	112.80
20	0.080	3.0 g. $BiCl_3$	0.93	0.92
21	0.155	3.0 "	0.93	0.93
22	0.155	3.0 "	1.86	1.85
23	0.155	1.0 g. $CdSO_4$	0.93	0.95
24	0.155	4.0 g. $CdCl_2$	4.65	4.55
25	0.155	4.0 "	4.65	4.48
26	1.0 g. $PtCl_4 4H_2O$	No salt	2.79	(2.36)
27	1.0 "	2.0 g. $SnCl_2$	2.79	2.77
28	0.300 g. Fe	2.0 g. $Pb(C_2H_3O_2)_2$	0.93	1.90
29	0.300 "	2.0 "	1.86	1.82
30	0.155 "	No salt	1.86	(0.99)

Numbers inclosed in parentheses ( ) show the retentive effect of salts of iron or platinum, when the salt of another metal is not added.

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[1] In experiment 17 the amount of arsenic recovered was slightly lower than it should have been. Since but 40 grams of zinc were used, in experiments 18 and 19 this amount was increased to 100 grams, and the size of the flask to one liter. Under these conditions no difficulty was experienced in the determination of more than a tenth of a gram of metallic arsenic, so this method could be used for the separation of arsenic from iron in ores containing arsenic.

It was found possible to make this separation with either arsenious or arsenic acid when the iron was added either in the ferrous or the ferric state, but the results given above were obtained in experiments where arsenious oxide alone was used.

In the preliminary experiments cadmium salts did not give such good results as when salts of tin were added. This seems due, in part, to the fact that the evolution of hydrogen was much less rapid in the former case. Bismuth salts are less easily purified, and lead salts produce an insoluble sulphate when sulphuric acid is used. For these reasons, most of the experiments were made with stannous chloride. The salts used were purified from arsenic, and all of the other reagents were also purified in cases where arsenic was present.

Good results were obtained by the electrolytic method in the absence of iron when as much as two milligrams of arsenic were present, but the addition of stannous chloride has not produced the same favorable result in the presence of iron as is obtained when the ordinary Marsh generator is used. When zinc electrodes are used in the presence of stannous salts the electrodes dissolve rapidly, so that the conditions are almost the same as those in the ordinary Marsh test.

It was considered possible that a part of the great retentive action of iron salts might be due to a chemical action between the iron salts and the arsine. To test this, the arsine produced in experiments such as those given in Table IV was passed through concentrated solutions of iron salts, with the result that no arsine was absorbed. This, of course, does not prove that compounds are not formed at the surface of the zinc in the generator.

In order to see if there is a connection between the excess potential of the metals and the reducing action of the hydrogen liberated from these metals in the Marsh generator, it was essential to determine a number of excess potentials previously undetermined. These determinations are now in progress, and nearly all of the common and rare metals which can be obtained in a suitable form have been procured for use in this work. The greatest difficulty experienced has been that of keeping the surface of the metals in a proper condition, and at the same time to eliminate the last traces of oxygen from the apparatus.[1]

Approximate determinations of the excess potential were first made by the method of Caspari. The results of these determinations, although made by a method which is only approximate in its results, are of some value in connection with the data presented. It is hoped that more accurate numbers can be presented in the second paper. It is universally recognized that the value of the excess potential of a metal depends to such an extent upon its surface condition and its previous condition as an electrode that it is impossible to obtain concordant values.

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[1] See Lewis and Jackson, *Z. physik. Chem.*, 56, 199 (1906).

TABLE V.—THE EXCESS POTENTIAL OF THE METALS IN VOLTS AS DETERMINED BY THE APPROXIMATE METHOD OF CASPARI.

	Excess potential in volts.		
Metal.	Caspari.	New determination.	Tafel.[1]
Mercury	0.78	0.74	1.30
Zinc	0.70	0.71	....
Lead polished	0.64	0.62	1.30
Lead rough	....	....	1.23
Tin	0.53	0.55	1.15
Cadmium	0.48	....	1.22
Arsenic	....	0.39	....
Bismuth	....	0.38	1.00
Copper	0.23	0.25	0.79
Cobalt	....	0.22	....
Nickel	0.21	0.15	0.74
Silver	0.15	0.13	0.93?
Gold	0.02	....	0.95
Iron	0.07	....	....
Platinum	0.09	0.07	....
Platinum black	0.005	0.002	0.07
Palladium	0.48	0.02	....
Palladium black	....	0.002	....

Temperature = 20° C.

A study was made of the variation of the excess potentials of bismuth and copper with the current density. The curves of excess potential follow in general the equation

$$E = A + B \log I,$$

in which A and B are constants. From the measurements of Caspari and of Tafel[2] it would seem that the values of B for silver and gold are greater than for nickel and platinum. This shows that it is unsafe to draw too definite conclusions as to the relationship between excess potential and the reducing action of hydrogen in the Marsh generator, until the curves of the variation of excess potential with the current density are more definitely determined. That other factors than current density influence the excess potential is shown by the results of Tafel upon the potential of a silver electrode. When the silver cathode was separated from the anode by a porous cell, the potential value for 0.125 ampere per sq. cm. and 2 N sulphuric acid was about 1.5 volts, while, when there was no separating wall between the anode and the cathode, the potential soon fell to 1.15 volts.

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[1] *Z. physik. Chem.*, 50, 712 (1904). The values given are for a current density of 0.1 ampere per square centimeter.

[2] *Z. physik. Chem.*, 50, 712 (1905).

It will be seen by referring to the values for the excess potential of the metals given in Table V, that those metals which were found favorable to the reduction of the oxides of arsenic to arsine are metals of high excess potential, while those which proved unfavorable were metals of low excess potential.

The one seeming exception to this rule, in the case where a salt of mercury was added, was due to the effect of the mercury in decreasing the speed of the solution of the zinc, just as would be expected when the zinc becomes coated with an amalgam whose excess potential is as great or greater than that of the zinc itself.

That the rapidity of the reduction and its completeness depended also upon the speed with which the hydrogen was evolved, and therefore upon the current density, was proved by varying the speed of solution of the zinc and weighing the arsenic deposited for a certain time interval.

The system used was so complicated that the experiments gave little light as to the catalytic effect of the different metals upon the reduction. That the electrolytic method is more favorable for the investigation of this problem is obvious. It is probable that the reduction of arsenious oxide to arsine takes place in two or more stages, and it is possible that an intermediate reduction product other than arsenic may be found.

When the iron was alloyed with the zinc used in the generator, it had the same injurious effect as if it were added to the solution as a salt,[1] and the addition of stannous chloride proved favorable as before.

If we consider the system previously discussed, that of platinum deposited upon zinc, it is to be expected that, on account of the lower excess potential of the platinum, the hydrogen given off will have a low reducing power. That the amount of arsenic reduced to arsine is less than that added to the generator was proved by a number of experiments, only one of which is listed in Table IV (Experiment 26). If a salt of tin is now added, the tin precipitates upon the platinum (and upon the zinc as well) and covers it in such a way that a new surface is substituted. If this new surface has the same excess potential as tin, the reduction should become more rapid than before. That this is the case has been proved in a number of instances.

When a salt of iron is dissolved in the solution the case is more complex, since practically all of the iron remains in solution, together with a part of the arsenic. Whatever may be the cause of the tendency of iron to prevent the reduction, it is probable that the beneficial action of the tin added is due to an increase of potential at the surface from which hydrogen is liberated.

The separation of arsenic from iron is extremely important in work where only traces of arsenic are present, for almost all substances which contain arsenic also contain small amounts of iron, and in no case is the zinc used free from iron. For this reason, whenever the Marsh method is used, the conditions should be such as are favorable to the separation of the arsenic from the iron which is always present.

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[1] Parsons and Stewart, *Loc. cit.*

The results of this work should not be understood to mean that the excess potential alone is the determining factor in the reduction, but only that it is one factor. A study of the electrolytic reduction of arsenic and arsenious acids will undoubtedly prove that certain metals of lower excess potential are more efficient cathodes for purposes of reduction than certain other metals of higher excess potential.

It is interesting to note that arsenic itself is a metal of moderately high excess potential, so that, if any arsenic were precipitated upon the zinc, the reducing action of the system would not be materially lessened. The addition of a solution of arsenic to the Marsh generator makes the zinc "active" without the addition of the salt of any other metal.

The fact that the value of the excess potential of the metal added to the generator has an influence upon the reduction, proves that at least one step in the reduction takes place at the surface of this metal, and that at least this part of the reduction is due, therefore, to the hydrogen and not to the zinc.

Summary.

1. The addition of salts of tin, cadmium, lead, or bismuth to the liquid in the Marsh generator makes the zinc "active" without the decrease in reducing power which comes from the platinum or iron commonly added as salts, or as alloys with the zinc.

2. Arsenic may be separated quantitatively from iron and determined in one process by either heating the generator or by adding a salt of one of the metals named above.

3. So far as has been investigated, metals of low excess potential hinder the reduction in the Marsh generator, while metals of high excess potential do not have any injurious action. However, it is not claimed that this will be a perfectly general relation, since the variation of other factors will undoubtedly be great enough to cause exceptions to the general rule.

4. The speed of the reduction of an oxide of arsenic increases with the rapidity of evolution of hydrogen, provided that the latter effect is not due to the addition of a metal of low excess potential; or the speed of reduction depends upon the current density. This is to be expected, since the current density is one factor in determining the electrode potential.

5. The determination of arsenic is made more accurate by the use of a special form of furnace for heating the glass tubes in which the arsenic is decomposed.

6. Since as much as 0.1 gram of metallic arsenic may be separated

from iron and determined quantitatively, this method is applicable to the analysis of ores and other substances containing large amounts of arsenic.

7. The method may also be used for amounts of arsenic as small as 0.001 milligram, but the apparatus must be made much smaller than that described.

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